CONTENT

LIST OF ABBREVIATIONS

A0	: PMMA homopolymer
A5	: Non-crosslinked copolymer with 5% macromer
A10	: Non-crosslinked copolymer with 10% macromer
A15	: Non-crosslinked copolymer with 15% macromer
A20	: Non-crosslinked copolymer with 20% macromer
A30	: Non-crosslinked copolymer with 30% macromer
AN	: Acid number
ANOVA	: Analysis of Variance
ATR	: Attenuated-Total Reflectance
B5	: Crosslinked copolymer with 5% macromer
B10	: Crosslinked copolymer with 10% macromer
B15	: Crosslinked copolymer with 15% macromer
B20	: Crosslinked copolymer with 20% macromer
B30	: Crosslinked copolymer with 30% macromer
BPO	: Benzoyl peroxide
DSC	: Differential Scanning Calorimetry
EGDMA	: Ethylene(glycoldimethacrylate)
FEPA	: Federation of European Producers of Abrasives (European grit guide for grinding papers)
FTIR	: Fourier-Transform Infra Red
ISO	: International Standard Organization
IV	: Iodine value
MMA	: Methyl methacrylate
PMMA	: Poly(methylmethacrylate)
PORIM	: Palm Oil Research Institute of Malaysia
S.D.	: Standard Deviation
SEM	: Scanning Electron Microscopy
TGA	: Thermogravimetric Analysis
W_{sl}	: Water solubility
W_{sp}	: Water sorption

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CHAPTER 1

INTRODUCTION

1.1 Vegetable Oils

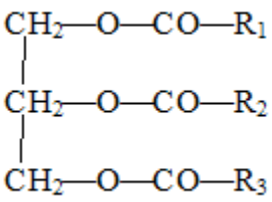
Recently, usage of renewable sources in various industrial fields has been revitalized because of environmental concerns. Industries are having increasing demands on natural products because of environmental issues such as waste disposal and depletion of non-renewable resources (Raquez et al., 2010, Jenck et al., 2004, Raquez et al., 2007, Kummerer, 2007, Raston, 2005, Frattini, 2008). Renewable resources can substitute partially or totally the petroleum-based polymers through the design of bio-based polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis with high eco-friendliness values (Raquez et al., 2010). Oils are renewable resources and the polymers prepared from them are biodegradable and, in many cases, cheaper than petroleum-based polymers (Koprolulu et al., 2008).

Vegetable oils are considered to be the most important class of renewable sources. They can be obtained from naturally occurring plants, such as sunflower, cotton and linseed (Guner et al., 2006). Plant oils are triglycerides (triesters of glycerols with long-chain fatty acids) with varying composition of fatty acid depending on the plant, the crop, season and growing conditions (Raquez et al., 2010). Plant oils have many advantages, apart from being a sustainable source; they are inexpensive, available in large quantities, easily processed, and

conveniently applied (Ikhuoria et al., 2005). Vegetable oils are used in a wide variety of industries ranging from soap manufacture to the production of paints, varnishes, lubricants and plastics. Some oils such as linseed, tung and castor oils have industrial applications only. Some others have both industrial and edible purposes; these include palm, palm kernel, soybean and coconut (Igwe, 2003).

1.2 Triglyceride Oils and Oil-based Polymers

Oils are triglycerides that are liquid at room temperatures, 28-30°C. They are water insoluble products of plants. A triglyceride is an ester obtained from one molecule of glycerol and three molecules of fatty acids (Figure 1.1). Triglyceride also can be produced from the reaction of glycerol and fatty acids (Figure 1.2).



R_1, R2 and R_3: Fatty acid chain

FIGURE 1.1 A triglyceride molecule.

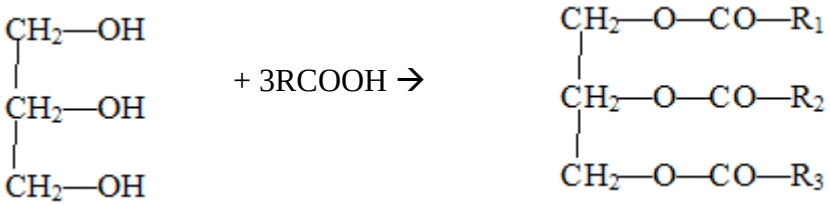


FIGURE 1.2 Synthesis of triglyceride.

The most common fatty acids in natural oil are palmitic acid, oleic acid, linoleic acid and palmitoleic acid to name a few. Some fatty acids are saturated and some of them are unsaturated. Saturated fatty acids have no double bond. In contrast, unsaturated fatty acids contain one or more double bonds and this characteristic gives different properties.

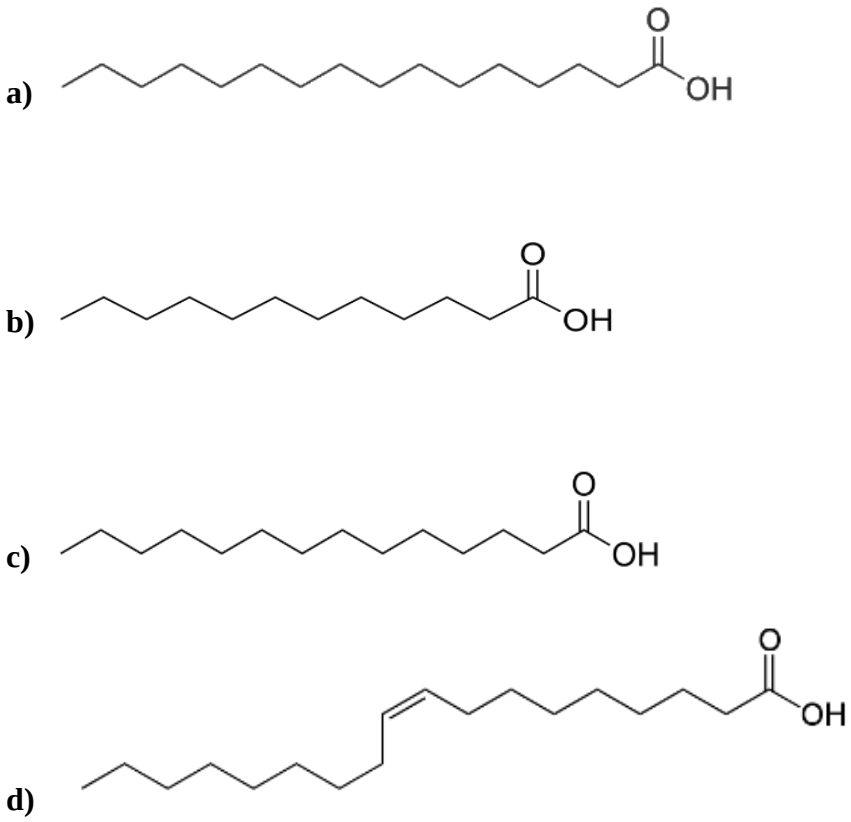


FIGURE 1.3 Saturated and unsaturated fatty acids commonly found in palm oil and palm kernel oil; a) Palmitic acid, b) Lauric acid, c) Myristic acid, d) Oleic acid.

In addition, natural fatty acids have different structures, with fatty acid molecules having hydroxyl, epoxy or oxo groups. Some fatty acid molecules also contain triple bonds. Their structural differences explain various physical properties that each fatty acid possesses.

Among the triglyceride oils, linseed, sunflower, castor, soybean, oiticica, palm and rapseed oils are commonly used for synthesis of oil-modified polymers. Although fatty acid pattern varies between many parameters, each of the triglyceride oils has special fatty acid distribution. Linseed oil, for example, consists of largely linoleic and linolenic acids while castor oil mainly consists of ricinoleic acid. Depending on the fatty acid distribution, each type of oil has specific physical and chemical properties. For example, linseed oil is used for the preparation of paint binder while castor oil is an important reactant for interpenetrating polymer networks (IPNs) because it contains hydroxyl groups that are capable to react with isocyanate and carboxyl groups (Guner et al., 2006).

Over the last few decades, the Malaysian palm oil industry has grown to become a vital agriculture-based industry (Yusoff, 2006). Technologies to produce oil-based polymers and resins from palm oil and palm kernel oil, that are economically competitive to petroleum-based polyols, have been developed in Malaysia (Velayutham et al., 2009, Hassan et al., 1993, Badri and Khairul, 2006, Ghazali et al., 2005).

One of the most dominant parameter affecting fatty acid and oil properties is the degree of unsaturation. The average degree of unsaturation is measured by iodine value. It is calculated from the amount of iodine (mg) reacted with double bonds for 100 g sample under specified conditions. Triglyceride oils are divided into three groups depending on their iodine values; drying, semi-drying and non-

drying oils. The iodine value of drying oil is higher than 130. This value is between 90 and 130 for semi-drying oils. If the iodine value is less than 90, the oil is referred to as non-drying oil (Guner et al., 2006).

Generally, a few drying and semi-drying oils, such as sunflower, soybean and linseed oils are used in the preparation of oil-modified polyesters. In addition, new vegetable oils, such as rubber seed, karinatta, orange seed and melon seed oils were also used for polyester resin synthesis (Igwe, 2003, Nair et al., 1881, Khandelwal and Gogte, 1976). In industrial practice, drying oils are most frequently used to form resins due to their high ability for auto-oxidation, peroxide formation, and subsequent radical polymerization, as currently applied in paint and coating formulations (Raquez et al., 2010).

1.3 Introduction of Polyester and Alkyd

Although the biggest usage of triglycerides is in the coating industry, in the last decade, triglyceride oil-based polymers have been used for many different applications. Some type of polymers prepared from triglyceride oils are oxypolymerized oils, polyesters, polyurethanes (urethane oils), polyamides, acrylic resins, epoxy resins and polyesteramides.

One of natural oil-based polymers is polyesters. Polyesters are among the most versatile synthetic polymers which have wide commercial applications as

fibers, plastics and coatings (Stevens, 1999). Polyesters are polymers which contain repeating units of ester group in their polymer chains (Figure 1.4).

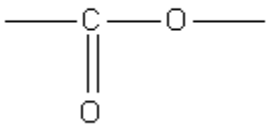


FIGURE 1.4 Ester linkages

In general, polyesters are produced by condensation of polyfunctional carboxylic acids (or their derivatives) with polyfunctional alcohols. Polyesters can usually be synthesized by the following four general synthetic routes: (i) Direct esterification of carboxyl groups with alcoholic hydroxyl groups, (ii) Transesterification (such as alcoholysis or acidolysis), (iii) Reactions of glycols or other polyfunctional hydroxyl compounds with anhydrides such as phtalic anhydride, (iv) Reaction of acid chlorides with glycols or bisphenols (Schotten-Baunmann reaction). Of these synthetic routes, the first three are more frequently used (Paul, 1985).

Ever since the last decade, synthesis and usage of biodegradable polymers have attracted wide attention, especially biodegradable polyesters that are useful materials for medical purposes (Slivniak and Domb, 2005). In this work, polyester of palm oil-based was utilized. There are several types of polyester which are linear polyesters, hyper-branched polyesters and cross-linked polyesters. Emphasis in this project will be on cross-linked polyesters which can be divided into two groups of saturated and unsaturated polyesters. Saturated polyesters are

those prepared from poly-functional monomers so that cross-linking occurs during the polyesterification reaction. The unsaturated polyesters are cross-linked by a separate addition polymerization reaction through reactive double bonds incorporated into the polyester backbone (Stevens, 1999).

1.4 The Alkyd

1.4.1 Origin of Alkyd

Alkyd resin is one of the oldest polymers prepared from triglyceride oils, produced by the esterification of polyhdroxy alcohols with polybasic acids and fatty acids. The preparation of polyester resin from tartaric acid and glycerin dated back as early as 1847 although the resulting polymer was brittle. In 1901 Watson and Smith used phthalic acid instead of tartaric acid. The resin was also not flexible. In 1914, Kienle used fatty acids in the preparation of polyester resin and the resulting alkyd resin exhibited good film properties (Guner et al., 2006).

Kienle was the first person to introduce the term alkyd (Patton, 1962) for any oil-modified polyester. It is a tough resinous product, formed through esterification where a polyacid reacts with a polyol and water is released as by product. The presence of fatty acid as a significant part of its composition distinguishes an alkyd from the other polyesters.

1.4.2 Classification of Alkyd

Generally, alkyd resins are classified into different oil length (OL) based on the content of oil (or fatty acid) in its formulation. This is shown in Table 1.1.

Table 1.1
Classification of alkyd resin

Alkyd resin	Oil or fatty acid (%)
Short oil length	Less than 45
Medium oil length	45-55
Long oil length	Over 55

OL refers to the percentage of oil in an alkyd formula. A short oil length alkyd contains less than 40% of oil. When oil amount increases between 45% and 55%, it is referred to as medium oil length and above 55%, the resin is a long oil length alkyd. OL is an important factor, which affects the properties of the final product (Bailey, 1996). Short oil alkyds are mostly used for baked finishes on automobiles, refrigerators, stoves, washing machines and etc. Long oil alkyds are used in brushing enamels along with any other applications (Guner et al., 2006) while medium oil length is largely considered responsible for its optimum durability.

As a group, alkyds are characterized by rapid drying, good adhesion, flexibility and durability. The choice of a resin for a particular use depends on a number of factors including performance, characteristics, processing

requirements, application properties and economic requirement (Ikhuoria et al., 2005).

1.4.3 Preparation of Alkyd

In most cases, monoglyceride and fatty acid methods are used to prepare alkyd resin. In the former case, the first stage is alcoholysis of the oil by a part of the polyol. Then, the free hydroxyls of the alcoholysis product are esterified by a polyacid.

1.4.4 Usages of Alkyd

Alkyd resins have acquired a good reputation because of their ease of application and they are not expensive. In addition, they are to a greater extent, biodegradable polymers because of the oil and glycerol parts (Guner et al., 2006). Alkyd resins are widely used in paint and coating industry due to their versatility and performances on metal substrates. Alkyd based coatings are well-known for fast drying, good corrosion protection, high gloss and the ease of application even over poorly treated surfaces (Gan and Teo, 1999).

Other field of alkyd resins application is as a component for offset printing inks (Blayo et al., 2001). The most commonly used alkyd resins in the printing industry are linseed and soybean oils-based resins. Guner et al. (2006) reported that for economical reasons, sunflower and rapeseed oils were utilized as oil components for printing ink formulations (Sabin et al., 1997b, Sabin et al.,

1997a). Resin manufacturers change the type of vegetable oils and proportion of polyhydric alcohols with polybasic acids to suit the application and to take into account the cost of raw material. Drying and performance characteristics of the resins also can be further improved by modification with acrylics, styrene, polyamide, silicone and phenolic resins (Challinor, 1991).

Alkyds play vast roles in paint, coating and printing ink industries for many years. However, the use of these biocompatible and renewable sources of natural oil alkyd in the dental field has not been explored. It is the objective of this work to investigate application of this palm oil based alkyd in the dental area.

1.5 Dental Materials and Denture Base Polymer

The science of dental materials involves a study of the composition and properties of materials and the way in which they interact with the environment in which they are placed (McCabe and Walls, 1998). Dental materials may be classified as preventive materials, restorative materials and auxiliary materials. Denture base polymers is sub-categorized under indirect restorative materials which means they are used extra orally, in which the materials are formed indirectly on casts or other replicas of the teeth and other tissues (Anusavice, 2003).

Denture base itself is that part of the denture which rests on the soft tissues and does not include the artificial teeth. Prior to 1940, rubber vulcanite was the most widely used denture base polymers, but it has its own demerits such as

difficulty to pigment and tends to be unhygienic due to the uptake of saliva. Since then acrylic resin is used universally for denture base construction (McCabe and Walls, 1998).

There are a list of properties that must be taken into account in making a good denture base material, such as the strength and durability, satisfactory thermal properties, processing accuracy and dimensional stability, chemical stability, insolubility in and low sorption of oral fluids, absence of taste and odor, biocompatible and etc. (Craig, 2002).

The current composite materials have good color and translucency, but much lower wear resistance than the silver amalgams, which they are designed to replace. The lifetime for anterior polymeric restorative materials is about 8 years, but for posterior amalgams, which have the time of use about 10-20 years. This seems to be a very short period (Bogdal et al., 1997). Regardless of this deficiency there are diverse substantial reasons, such as esthetics and avoidance of mercury pollution of the environment, which spurred their further development (Sideridou et al., 2002).

Acrylic prosthetic resins are used in a number of types of dental prostheses, including complete or removable partial dentures, transitional prostheses and implant-supported prostheses. Most prosthetic acrylic resins consist of PMMA resin and additional copolymers, such as

poly(butylmethacrylate) or butadiene styrene. Cross-linking agents such as ethylene(glycoldimethacrylate) (EGDMA) and inclusions of rubber or fibers are added to modify their mechanical properties. The additives serve to improve toughness, impact resistance and to prevent crack propagation (Diaz-Arnold et al., 2008).

Denture bases are composed of pre-polymerized PMMA or poly(ethylmethacrylate) (PEMA) powder particles along with peroxide initiator and pigment, which are mixed with methacrylate monomers such as MMA, hexamethylene(glycoldimethacrylate), hydroxyl(ethylmethacrylate), n-butyl(methacrylate), tetra(hydrofurfuryl methacrylate) and cross-linking agents such as EGDMA, trimethylol(propanetrimethacrylate) or 1,6-hexanediol(dimethacrylate) (Bettencourt et al., 2010).

PMMA is the most common acrylic resin, a non-resorbable polymer and has been used in dentistry since 1930's as denture material and in medicine since 1950's as bone cement. When used as a denture base material, the powder-like polymerized PMMA beads are mixed with methacrylate liquid monomers containing a small percentage of dimethacrylate crosslinker.

It is superior to other materials in terms of aesthetics, easy handling and low cost. However, denture base should possess high mechanical strength in order to withstand fracture due to masticatory force or accidental damage (Darbar et al., 1994). The bond strength of PMMA composites have been studied by peel, tensile

and shear tests. It has been reported that the bond strength can be improved by modifying the surface topography of PMMA (Craig, 2002, Al-Athel and Jagger, 1996).

In general, it has excellent aesthetic properties, low water absorption and solubility, adequate strength, can be easily repaired and reproduced and able to retain the details and dimensions of a pattern. Resistance to impact fracture and high flexural strength are crucial desirable properties of denture base polymers. Mechanical properties of PMMA based denture base materials however are often insufficient for clinical use (Mjor, 1985) or in specific, as denture bases therefore opens room for further enhancement.

Biocompatibility is another desirable property for a dental polymer and it can be achieved by utilizing more materials from natural sources. During the polymerization reaction of the acrylic resins, the conversion of monomer into polymer is not complete and varying amounts of free or un-reacted monomer remain in the polymerized resin (Vallittu et al., 1998). Residual monomer (RM) can behaved as plasticizer and can affect the physical and mechanical properties of the acrylic resins. In addition, there have been descriptions of clinical cases in which the RM was found to be the cause of mucosal damage (Azzarri et al., 2003). It has been reported that a decrease in the RM content could be achieved by immersing conventional acrylic resins in hot water (Lamb et al., 1982, Tsuchiya et al., 1994) or using microwave irradiation (Arajo et al., 2002, Blagojevic and Murphy, 1999).

Polymeric denture base materials are classified into five groups (or types), as shown in Table 1.2 (McCabe and Walls, 1998).

Table 1.2
Classification of denture base polymers according to ISO 1567: 1999.

Type	Class	Description
1	1	Heat-processing polymers, powder and liquid
1	2	Heat-processed (plastic cake)
2	1	Autopolymerized polymers, powder and liquid
2	1	Autopolymerized polymers (powder and liquid pour type resins)
3	-	Thermoplastic blank or powder
4	-	Light-activated materials
5	-	Microwave-cured material

These denture base materials are classified according to ways of the processing. There are heat processed, auto polymerized, thermoplastic, light-cured and microwave-cured resins. Heat processed or heat-polymerized denture base resins are the most widely used material in the fabrication of acrylic denture. Thermal energy required for this purpose may be supplied using a water bath or microwave oven.

1.6 Choice of Raw Materials

1.6.1 Palm-oil based Macromer

In this study, one specific alkyd or macromer namely FA35 was used. This macromer, made from a mixture of palm kernel oil (PKO), palm oil, glycerol and phthalic anhydride (PA) has gone through process of alcoholysis and esterification. Generally, alcoholysis is a process of converting the immiscible polyol and triglyceride phases into a single homogenous monoglycerides phase. In this step, glycerol was added into PKO in the presence of certain catalyst, and the triglyceride oil was converted to the monoglyceride during alcoholysis. Subsequently, PA was added to monoglyceride in the esterification process. Fumaric acid was added together with PA later, to introduce higher a small level of unsaturation i.e. unit with C=C bonds. This macromer will copolymerize with MMA to be used in dental application. The target was to react the unsaturation of the alkyd with MMA to produce copolymer with branching.

1.6.2 Methyl methacrylate, MMA and poly(methyl methacrylate), PMMA

MMA is a monomer prepared from acetone through cyanohydrin route, the cyanohydrin is treated with 98% sulfuric acid in a cooled kettle to yield methacrylamide sulphate intermediate, which upon esterification with methanol, produces MMA (Figure 1.5). MMA is readily available commercially. It has a pungent odor and is a transparent liquid at room temperature. MMA is extremely volatile and readily polymerize in the presence of ultraviolet light, heat or free-radical yielding initiators. It freezes at approximately -50°C, boils at 100.8°C and

has a density of 0.943g/cm^3. Polymerization of MMA produces PMMA (Figure 1.6).

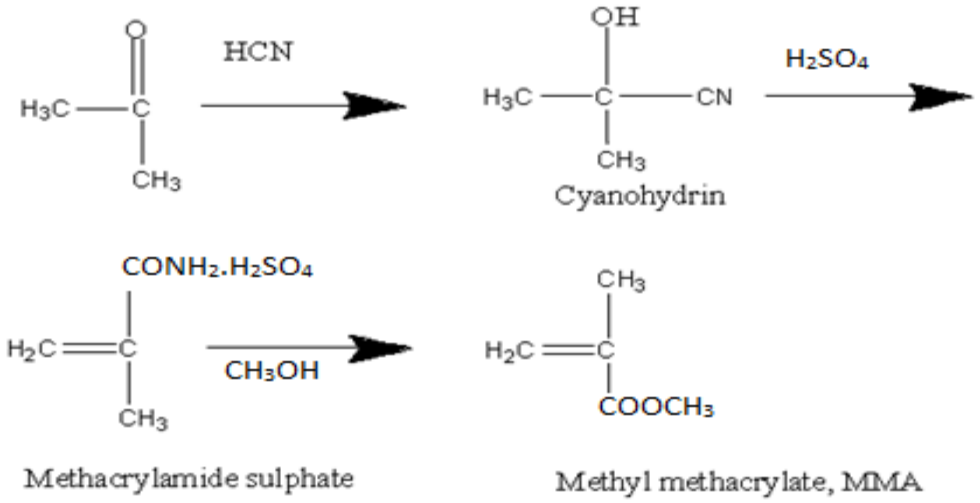


FIGURE 1.5 Commercial syntheses scheme of MMA.

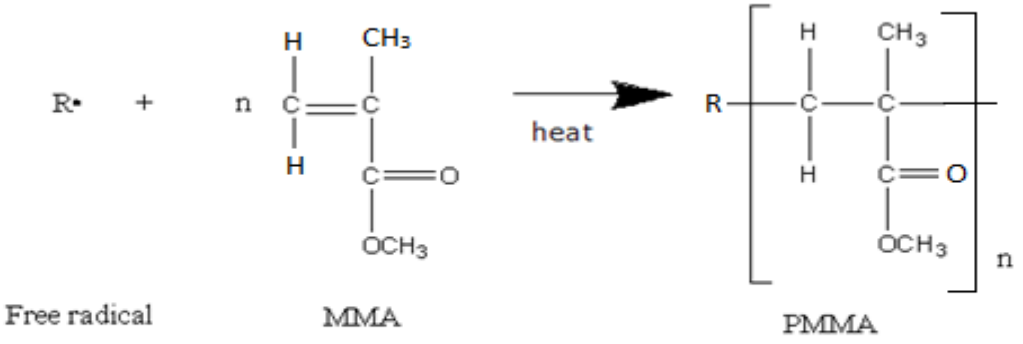


FIGURE 1.6 Free radical polymerization of MMA.

1.7 Free radical copolymerization

Most vinyl polymer including MMA undergoes free radical polymerization. Benzoyl peroxide (BPO) was used as the initiator and it is thermally unstable and decomposes into radicals at a certain temperature (Stevens, 1999). Figure 1.7 illustrated (a) Proposed reaction mechanism of free radical copolymerization of MMA and unsaturated macromer, and (b) Proposed reaction mechanism of free radical copolymerization of MMA onto macromer chain, showed plausible grafting.

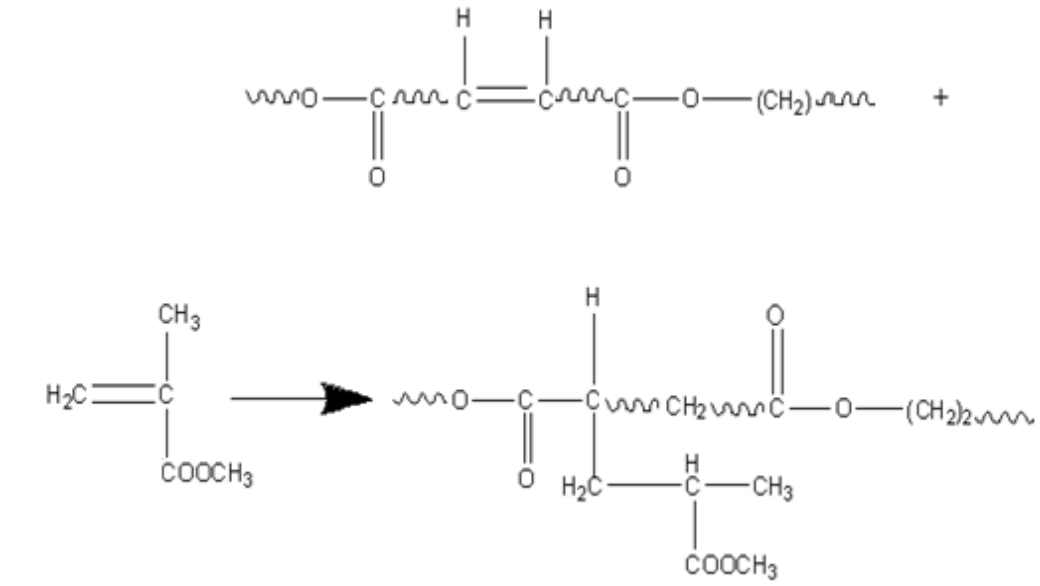


FIGURE 1.7 (a) Proposed reaction mechanism of free radical copolymerization of MMA and unsaturated macromer.

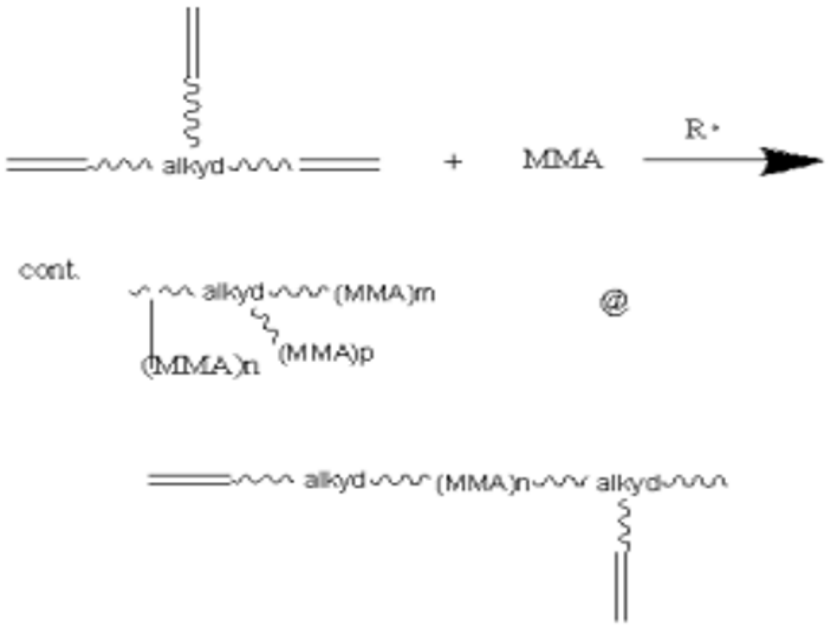


FIGURE 1.7 (b) Proposed reaction mechanism of free radical copolymerization of MMA onto macromer chain, showed plausible grafting.

1.8 Solution and bulk polymerizations

Solution polymerization of monomer is done in the presence of a diluent miscible solvent in all proportions with the monomer (Ghosh, 2002). The solvent reduces viscosity gain with conversion, allows more efficient agitation and stirring of the medium, thus affecting better heat transfer and heat dissipation. It also minimizes or avoids local overheating of the system or heat accumulation. Besides, it may also allow longer chain to be formed. This technique was chosen due to the stability of the reaction condition to copolymerize the two different components i.e. the macromer and MMA.

On the other hand, in terms polymerization recipe, bulk polymerization provides the simplest system, requiring the use of a very low concentration of initiator as the only additive in the monomer. However, the reaction is highly exothermic and heat dissipation must be addressed carefully. Heat dissipation could give rise to the monomer-polymer viscosity thus limits the use of bulk method in commercial production. MMA however could be polymerize using this method because of its simplicity and the heat dissipation problem is kept to a minimum and within tolerable limit by accomplishing the polymerization of macromer and MMA in stages. The initial stage is to obtain 20-30% conversion in a stirred reactor at 80-100°C and subsequently allowing the monomer-polymer syrup (viscous mass) poured in an appropriate mould assembly to polarize to (near) completion at progressively higher temperatures in stages (Ghosh, 2002).

1.9 Scope of Study

1.9.1 The Copolymerization

The MMA/PMMA copolymer system have been used widely in many application such as in textile (Enomoto et al., 2010), water purification/ adsorbent (Zeng et al., 2010), blends (Khalf et al., 2010), composites (Preda et al., 2008), dental and many more as copolymer, grafting system, interpenetrating networks (IPNS) and compatibiliser to name a few.

PMMA also has been reacted or blended with many synthetic and natural polymers such as poly(butyl acrylate), poly(methyl acrylate) (PEMA), acrylic acid, poly(vinylidene fluoride) (Gallagher et al., 1991), glycopolymers (Haddleton

and Ohno, 2000), cellulose diacetate and among others, with the purpose of increasing hydrophobicity, chemical and physical resistance of the new material (Haddleton and Ohno, 2000, Choi and Stansbury, 1996, Brar and Dutta, 1998, Juergen et al., 2000, Elizalde-Pena et al., 2007).

Notwithstanding many studies that have been carried out on fiber-reinforced plastics (Ruyter et al., 1986) to improve the mechanical properties of acrylic resin, they have been hindered by difficulties in overcoming problems of aesthetics and manipulation (Schreiber, 1971, Braden et al., 1988). Usage of natural polymers such as chitosan has been attempted to improve their mechanical properties (Sarasam and Madihally, 2005, Mahdavinia et al., 2004, Flores-Ramirez et al., 2005).

This project is designed to improve the properties of PMMA with incorporation of FA35 macromer. The copolymerization of MMA and macromer was made using two different techniques which were solution and bulk polymerization techniques.

1.9.2 Characterization of FA35 macromer and copolymers

The macromer and the copolymer produced were later characterized and compared with the homopolymer and commercial denture base resin. First, analysis was done using Fourier Transform Infra-Red (FTIR) followed by thermal analysis using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

1.9.3 Evaluation of copolymer as denture base material

Three properties of the copolymers as denture base polymers were evaluated according to ISO 1567:1999 specifications; Denture Base Resin.

Water sorption and solubility

The sorption of water alters the dimensions of acrylic dentures. This change in dimension is reversible, for the most part and the plastic may go through numerous expansions and contractions when alternately soaked and dried (Craig, 2002). This is apparently undesirable. Although denture base resins are soluble in a variety of solvents, they are virtually insoluble in the fluids commonly encountered in the oral cavity (Anusavice, 2003). Therefore, copolymer tested must conform to the limit established in the ISO specification as listed in Table 1.3.

Flexural strength and deflection

In the evaluation of denture plastics, transverse/flexural strength or modulus of rupture as it is called, are used to a greater extent than either tensile or compressive strength because this test more closely represents the type of loading in vivo. Flexural strength is determined by applying an increasing load until fracture occurs at the center of the test specimen. The deflection in millimeters at the middle of the plastic specimen is recorded at a maximum load where the plastic break into two pieces (Craig, 2002).

Impact strength

Impact strength is a measure of the energy absorbed by a material when it is broken by a sudden blow. Ideally, a denture base plastic should have

sufficiently high impact strength to prevent breakage on accidental dropping, but not at the expense of the other properties (Craig, 2002).

Table 1.3 summarizes the requirement of physical and mechanical properties of a denture base resin.

Table 1.3
Summary of the limit for the requirements of denture base polymer in accordance to ISO 1567 specifications.

Requirement	Flexural strength, MPa [min.]	Flexural modulus, GPa, [min.]	Sorption, $\mu g/mm^3$ [max.]	Solubility, $\mu g/mm^3$ [max.]
Type 1,3,4,5	65	2	32	1.6
Type 2	60	1.5	32	8.0

Reproduced from ISO 1567:1999 Denture Base Polymer Specifications

This type of polymer denture base is according to classification by ISO 1567: 1999 and in this work, the product copolymer is categorized to Type 1, Class 2; heat-processed (plastic cake) type denture base polymer.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

FA35 macromer was obtained from Rovski Sdn. Bhd. (Malaysia). It is a macromer made from PKO, glycerol, phthalic anhydride and fumaric acid. It has an acid value of about 45 mg KOH/g and iodine value of about 10 g iodine/100 g alkyd. Benzoyl peroxide (BPO), methyl methacrylate (MMA) and ethylene (glycol dimethacrylate) (EGDMA) were from Merck and Sigma-Aldrich (Germany). MMA was freed from stabilizer prior to use, and BPO was re-crystallized before usage. Commercial denture base powder and liquid were from Denstply Trubyte (USA). All other reagents used were of analytical grade and used as received.

2.2 Apparatus

Figure 2.1 shows the schematic drawing of apparatus used in the copolymerization with the presence of the solvent. Mechanical stirrer is used to supply agitation to the system. A condenser is used to minimize the evaporation of the reactants and a water bath is heated to supply heat for copolymerization in the range of 70-90°C.

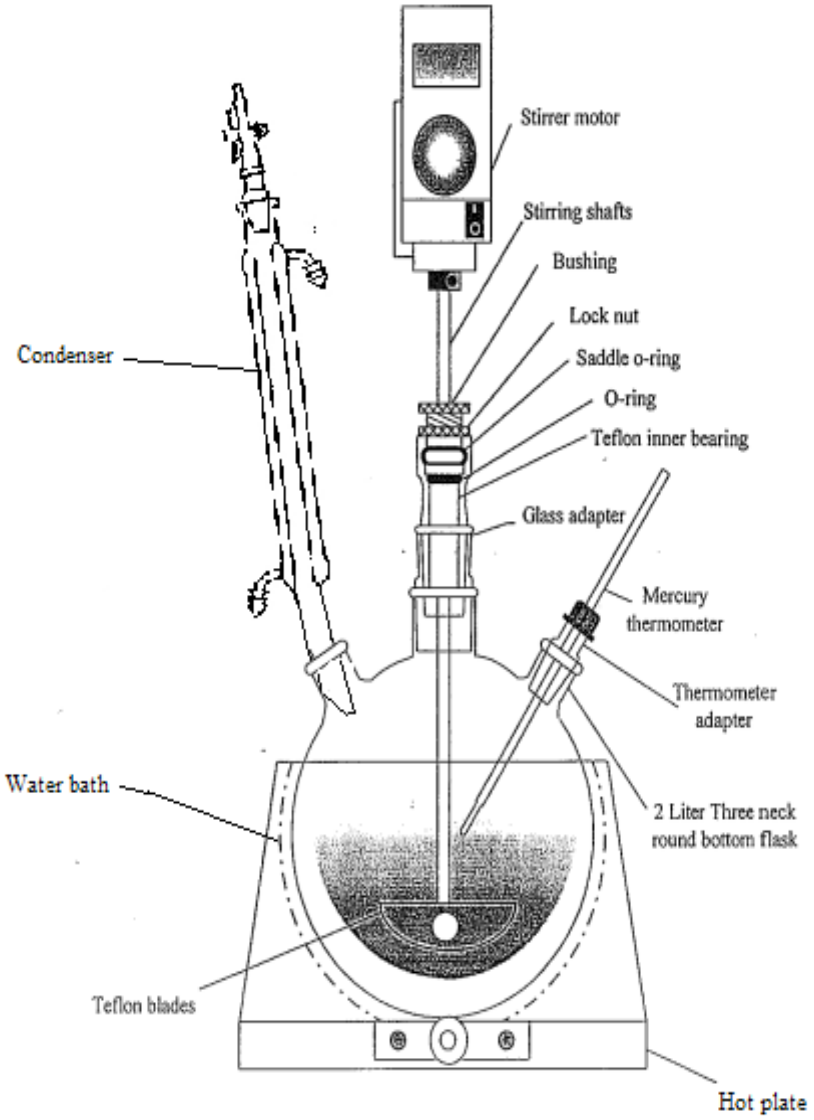


FIGURE 2.1 Apparatus for solution polymerization.

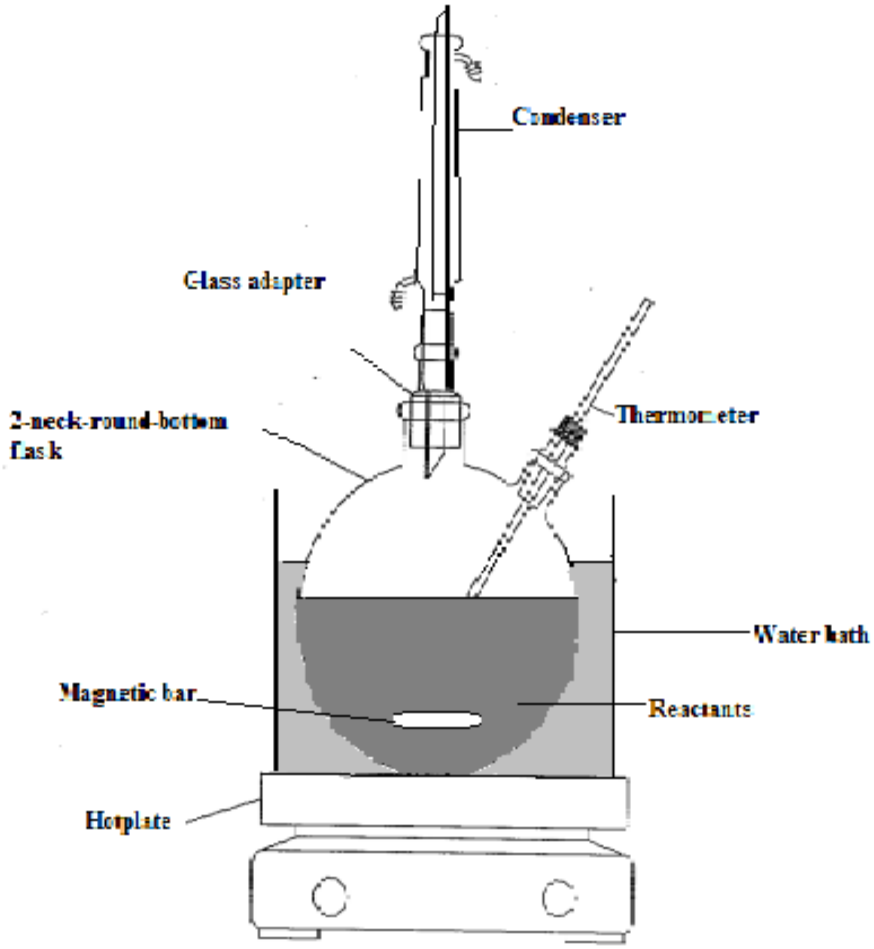


FIGURE 2.2 Apparatus for bulk polymerization.

Figure 2.2 shows the apparatus used for bulk polymerization of macromer and MMA. A heated water bath is used to supply heat to the reactants within the range of 60-70°C. The reactants were agitated using a magnetic bar due to the relatively small amount of reactants compared to the solution process. A condenser is also used to minimize the evaporation of the reactants.

2.3 Characterization of FA35 macromer

2.3.1 Determination of acid number (PORIM Test Method)

This test follows the PORIM test method (Siew et al., 1995b) with minor modifications to suit the experimental conditions. Acid number is defined as the number of milligrams of potassium hydroxide (KOH) necessary to neutralize the free fatty acids in 1 g of alkyd / macromer.

Standardization of KOH solution was carried out prior to the determination of acid number. A small amount of potassium hydrogen phthalate (KHP) was weighed into a conical flask. 50 mL water and a few drops of phenolphthalein indicator of 1% w/v were added. It was swirled until the salt had completely dissolved. After that, the solution was titrated with 0.08 N of KOH solutions until the first appearance of a permanent pink color. The normality, N of the KOH solution was calculated as follows:

N : (W x 1000) / (V x 204.2),

where W : weight of KHP taken (g)

V : volume of KOH used to titrate phthalate solution (mL)

204.2 : equivalent weight of KHP (g)

0.5 g of macromer was weighed and dissolved in 50 mL 95% v/v ethanol. The solution was heated and swirled on a hot plate until it has completely dissolved. A few drops of phenolphthalein indicator were then added. The mixture was titrated with standardized 0.08 N KOH solutions until the first appearance of a permanent pink color, which must be lasting for at least 30 seconds. Two replicates of FA35 macromer were prepared.

The acid value, AN, of the macromer was calculated by using the following formula:

AN = 56.1 x N x (V) / W,

where N : normality of KOH solution (N)

W : weight of sample (g)

V : volume of KOH solution used for the sample titration (mL)

2.3.2 Determination of iodine value (PORIM Test Method) (Siew et al., 1995c)

Preparation of Wijs reagent

9 g of iodine trichloride was weighed in a brown glass bottle of 2.5 L capacity. A mixture of 700 mL glacial acetic acid and 300 mL carbon tetrachloride was added. Subsequently, 5 mL of the solution was taken. 5 mL of the potassium iodide solution and 30 mL of water was added. The liberated iodine was titrated with 0.1 N sodium thiosulphate ($Na_2S_2O_3$) solutions in the presence of a few drops of starch indicator.

10 g of pure re-sublime iodine was added to the bulk reagent and was dissolved by shaking. The free iodine was titrated as above. The titre now equals to almost one and a half times that of the first reading. It is important that no trace of whatever iodine trichloride should remain as it would cause secondary reactions.

The solution was left to stand. The clear liquid was decanted into a brown glass bottle and was stored in a well-stopper bottle, away from light. The solution could be used for several months.

Standardization of sodium thiosulphate solution

Standard potassium dichromate ($K_2Cr_2O_7$) solution, 0.1 N was made by dissolving 1.2259 g of dried $K_2Cr_2O_7$ in distilled water and was made up to 250 mL in a volumetric flask. Subsequently, 25 mL of the standard $K_2Cr_2O_7$ solution (0.1 N) was pipetted into a conical flask. 5 mL of concentrated sulphuric acid and 10 mL of 10% potassium iodide solution was added and was swirled to mix. The solution was then left to stand for 5 minutes and then 100 mL of distilled water was added. Then, it was titrated with $Na_2S_2O_3$ solution and was shaken continuously until the yellow color has almost disappeared. After that, 1-2 mL of 1.0% w/v starch indicator was added and titrated continuously until the blue color disappeared.

Procedure of determination of iodine value

The macromer was warmed at 60 – 70 °C prior taking a test portion to get it flowing freely compared to its original viscous-condition. 0.42 g of the macromer was accurately weighed using analytical balance (Denver Instrument Co., US) in a 250 mL conical flask. 15 mL of carbon tetrachloride was added in the flask to dissolve the oil. Subsequently, 25 mL of the Wijs reagent was added. The stopper was placed and the flask was shaken gently and was left to stand in the dark for 1 hour. Then, 20 mL of the 10% potassium iodide solution and 150

mL of distilled water was added. The solution was titrated with $Na_2S_2O_3$solution until the yellow color due to iodine has almost disappeared. 1-2 mL of the 1% starch indicator solution was added and the titration was continued until the blue color was disappeared after vigorous shaking. Two determinations of FA35 sample were carried out. Beside that, a blank test was carried out simultaneously under the same condition.

2.3.3 Determination of relative density (PORIM Test Method) (Samaraweera, 1992 #137}

A specific gravity bottle was first cleaned and dried thoroughly for the purpose of calibration. The calibration was carried out at ambient temperature with distilled water. The empty bottle with its stopper was weighed and recorded as W_b. Next, the bottle was filled with freshly-prepared distilled water. The water was allowed to overflow into the bottle to prevent the entrapment of air bubbles. Then the stopper was placed. Water that has exuded from the capillary opening was carefully removed. The bottle was wiped dry completely and it was weighed with its content to the nearest 0.1 mg. It was recorded as W_w. This procedure was repeated using FA35 macromer. The weight of the bottle with the macromer was recorded as W_s. Two determinations were carried out in a rapid succession.

2.3.4 Determination of volatile matter content (PORIM Test Method) (Siew et al., 1995a)

The macromer was heated at 50 - 60°C prior to taking a test portion. A clean petri dish was dried in the oven at 103°C for 30 minutes and was allowed to cool in a dessicator. The dish was weighed using analytical balance (Denver Instrument Co., US). 10 g of warm macromer was put into the dish. Then the dish was returned to the dessicator until the oil has thoroughly cooled. The dish with the macromer was weighed to the nearest 0.1 mg and was placed in the middle shelf of the oven at 103°C for 2.5 hours. The dish was then removed and was allowed to cool thoroughly in the dessicator for 45 minutes before re-weighing to the nearest 0.1 mg. Three determinations were carried out simultaneously.

2.4 Copolymer formulation

2.4.1 Solution technique

Table 2.1
Formulation of MMA and macromer copolymerizations at 80°C of solution technique - S series.

Sample	Macromer /g	MMA/g	Toluene/g	BPO/g	Macromer: MMA
S1	20	20	40	2(2.4%)	1.00
S2	20	20	20	4(6.3%)	1.00
S3	20	20	30	2(2.8%)	1.00
S4	20	20	30	2(2.8%)	1.00
S5	20	30	20	2(2.8%)	0.67
S6	20	30	30	2(2.4%)	0.67
S7	20	30	30	2(2.4%)	0.67
S8	20	40	30	2(2.2%)	0.50
S9	20	40	40	2(2.0%)	0.50
S10	20	40	40	2(2.0%)	0.50
S11	20	40	50	4(3.5%)	0.50
S12	20	40	40	4(3.8%)	0.50
S13	20	45	40	2(1.9%)	0.44
S14	20	45	40	2(1.9%)	0.44
S15	20	45	40	4(3.7%)	0.44
S16	20	45	40	4(3.7%)	0.44
S17	20	45	30	2(2.1%)	0.44
S18	20	45	30	2(2.1%)	0.44
S19	20	45	30	4(4.0%)	0.44
S20	20	45	30	4(4.0%)	0.44

Item colored yellow indicates the addition of initiator with solvent was done half the amount prior to mixing and the other half was added after 1-2 hours of mixing.

Table 2.1 shows 20 compositions of starting materials for copolymerization using toluene as solvent. The objective of S series was to observe the nature of polymerization between the macromer and MMA. Reaction temperature was fixed at 80°C. The correlation between amount of the reagents and the reaction time with the yield of copolymerization were to be observed. For example, sample S3 and S4 had similar percentage of reactants composition but differed in the addition of initiator. In sample S3, all the initiator was added in the beginning of the reaction. On the other hand, for sample S4, initiator was divided into two portions and was added half the amount prior to mixing and the other half was added after 1-2 hours of mixing. The similar condition was set to sample S7 & S6, S9 & S10, S13 & S14, S15 & S16, S17 & S18 and S19 & S20.

For this series, amount of macromer was fixed to 20 g in each formula (18 wt% to 31 wt%) while monomer amount was increased from 20 g to 45 g (or 24 wt% to 46 wt%). Amount of toluene used was of 20 – 50 g (30 wt% to 48 wt%) and initiator used was from 2 g to 4 g (2 wt% to 6 wt%). Samples S13 to S16 and samples S17 to S20 consisted of the same amount of MMA and monomer (reactants) respectively and differed only in addition of BPO.

Table 2.2
Formulation of J series, copolymerizations of macromer with MMA at 80°C with fixed amount of initiator and solvent.

Sample	Macromer /g	MMA /g	Toluene /g	BPO /g	Macromer: MMA	Reactant: solvent
J1	20	10	20	2	2.00	1.50
J2	19	11	20	2	1.73	1.50
J3	18	12	20	2	1.50	1.50
J4	17	13	20	2	1.31	1.50
J5	16	14	20	2	1.14	1.50
J6	15	15	20	2	1.00	1.50
J7	14	16	20	2	0.88	1.50
J8	13	17	20	2	0.76	1.50
J9	12	18	20	2	0.67	1.50
J10	11	19	20	2	0.58	1.50
J11	10	20	20	2	0.50	1.50

Toluene is 38.5 wt% and BPO is 3.8 wt%.

Table 2.3
Formulation of L series, copolymerizations at 90°C with fixed amount of initiator and solvent.

Sample	Macromer /g	MMA /g	Toluene /g	BPO /g	Macromer: MMA	Reactant: solvent
L1	20	10	20	2	2.00	1.50
L2	19	11	20	2	1.73	1.50
L3	18	12	20	2	1.50	1.50
L4	17	13	20	2	1.31	1.50
L5	16	14	20	2	1.14	1.50
L6	15	15	20	2	1.00	1.50
L7	14	16	20	2	0.88	1.50
L8	13	17	20	2	0.76	1.50
L9	12	18	30	2	0.67	1.00
L10	11	19	30	2	0.58	1.00
L11	10	20	30	2	0.50	1.00

The J and L series were formulated to investigate the copolymerization at two different reaction temperatures, which were 80°C and 90°C respectively. Table 2.2 shows decrease of macromer amount and increase of MMA from sample J1 until Sample J10. The solvent was fixed at 38.5 wt% of reaction mixture and BPO was fixed at 3.8 wt%.

Table 2.3 also shows reduction of macromer amount from 39 wt% to 16 wt% and a raise of MMA amount from 19 wt% to 32 wt%, seen from Sample L1 until Sample L10. The solvent was fixed at 39 wt% and 48 wt% and BPO was fixed at 3.2 wt% and 3.8 wt% of total reactants.

2.4.2 Bulk technique

Table 2.4
Formulation of bulk copolymerizations of macromer and MMA - Bulk A series.

Sample	Macromer/g	MMA/g	BPO/g	Macromer: MMA
A0	0	225.0	1.0	0.00
A5	12.5	237.5	1.0	0.05
A10	25.0	225.0	1.0	0.11
A15	37.5	212.5	1.0	0.18
A20	50.0	200.0	1.0	0.25
A30	67.0	167.0	1.3	0.40

Table 2.4 shows 6 formulations of bulk copolymerization technique with no addition of crosslinking agent and formulation for homopolymer (control). The macromer amount was increased from 5 to 30 wt% while MMA amount was decreased from 95 to 70 wt% (macromer to MMA ratio was increased). Initiator was fixed at approximately 0.4 to 0.6 wt% of total monomer. The purpose of these bulk series was to obtain a good copolymer, which is hard, free from air bubbles and is acceptable for physical and mechanical testings.

Table 2.5
Formulation of bulk copolymerizations of macromer and MMA with crosslinker addition - Bulk B series.

Sample	Macromer/g	MMA/g	BPO/g	EGDMA/g	Macromer: MMA
B5	12.5	237.5	1.0	0.625	0.05
B10	25.0	225.0	1.0	0.625	0.11
B15	37.5	212.5	1.0	0.625	0.18
B20	50.0	200.0	1.0	0.625	0.25
B30	75.0	175.0	1.0	0.625	0.43

BPO is 0.4 wt% and EGDMA is 0.25 wt%.

Table 2.5 shows 6 formulations of bulk copolymerization technique with crosslinking agent addition of 0.25 wt% of total monomer. The macromer amount was increased from 5 to 30 wt% and MMA amount was decreased from 95 to 70 wt%. Initiator was fixed at 0.4 wt% of total monomer.

2.4.3 Commercial denture base resin

Commercial denture base resin came in a set of pre-polymer PMMA powder and MMA monomer. It was mixed with certain crosslinking agent and fillers. The commercial resin used for comparison purposes was Lucitone 199® (Dentsply Trubyte, USA). They were applied according to the manufacturer's instructions. Generally, 1 unit of powder (about 21 g) was added to 10 mL monomer. The formulation was scaled to produce a polymer to fit in a selected mold.

2.5 Synthesis of copolymer, homopolymer and commercial denture base polymers.

2.5.1 Solution polymerization technique

The solution copolymerization of MMA with FA35 macromer was carried out in several series. In the beginning, the series were held to study the nature of copolymerization of macromer with MMA, with the objective to obtain high yield. After getting a high yield formulation, the study moved to other technique of synthesis.

The polymerizations of S, J and L series were carried using different formulations but generally using the same method. The macromer was mixed with MMA to form a homogenous solution in a reaction flask. Next, initiator was dissolved in toluene and was added into the reaction flask using dropping funnel prior to mixing (unless stated otherwise for certain samples in the S series). Subsequently, this mixture was heated to 80°C for J series and 90°C for L series. The copolymerization was done for 7 to 9 hours in a water bath.

Copolymer was precipitated out using methanol at five times the amount of copolymer solution. The precipitated polymer was isolated by filtration and was dried for 2 days at 100°C. For mechanical testing purposes, the copolymer was re-dissolved in a minimum amount of solvent, cast into a plate form and dried again at gradually increasing temperature from 40°C to 110°C over two days to avoid bubble formation when the solvent evaporated. Then, it was sectioned using a precision diamond saw (Buehler, Germany) to form specimens needed according to the designated test. PMMA homopolymer was prepared using the

same method as described using MMA monomer alone without macromer. Yield of each reaction was determined gravimetrically.

2.5.2 Bulk polymerization technique

In bulk technique, two main series were formulated, namely Series A and B. Both were series of copolymers without and with crosslinking agent respectively. This technique has MMA acted as a monomer and the liquid medium of polymerization. Copolymer was made by mixing MMA with macromer in a 250 mL-round-bottom reaction flask using magnetic stirrer. BPO was added and stirred to dissolve in the mixture at ambient temperature.

For series with crosslinking agent (Series B), initiator and crosslinking agent, EGDMA were mixed with MMA before the mixture was added with macromer and stirred. After that, the reactor flask was put into a water bath set at 50°C-60°C and was stirred slowly using magnetic stirrer. The viscosity of the reaction mixture was monitored carefully.

After about an hour, the temperature was raised to 70°C and the viscosity of the mixture was continuously monitored. When the mixture turned viscous, it was transferred into a polypropylene mold at 60°C. Then the mold, covered loosely with a lid to avoid overheating, was maintained at 60°C overnight for the reaction to complete. Subsequently, it was put into an oven at 100-110°C for 3 to 4 hours to remove trace amount of un-reacted monomer. The polymer syrup was stirred at 60 – 70°C for total reaction time varied from 4 to more than 7 hours. Higher weight percent of macromer would require shorter time for the copolymerization.

The copolymer was light yellow in color, taking the color of the macromer. The sample was cooled to room temperature and was removed from the mold. PMMA homopolymer of bulk polymerization was prepared using the same method as described without macromer. Yield of each reaction was determined gravimetrically.

FIGURE 2.3 Pre-polymer syrup inside a polypropylene mold is put in water bath to cure at 60-70°C overnight.

2.5.3 Commercial denture base polymer

Specimens for commercial denture base resin namely Lucitone 199® was prepared according to the manufacturers' instructions and test specimens were prepared according to the procedure of the standard test method.

FIGURE 2.4 Commercial denture base resin packaging, liquid and powder Lucitone 199®.

Lucitone 199® preparation procedure

The resin powder and liquid were measured accurately.

1. MIXING

To assure color uniformity, powder jar was shaken using a rocking motion to prevent concentration of small particles resides at the bottom of the container. 1 unit powder of 21 g was added to 10 mL liquid. Mixture was stirred for 15 seconds to ensure wetting of all powder particles. The mixing container was covered and the material was left for approximately 9 minutes at room temperature of 28±1°C until the resin became not sticky.

2. PACKING

The resin was packed in a jar at room temperature (28 - 31°C). The correct packing consistency was identified when the resin dough is free from stickiness but not rubbery. Resin dough then was removed from the jar and was condensed with finger pressure into mold.

3. WORKING TIME

The working time i.e the time used for mixing and packing processes of the resin was approximately 10 minutes. Thus packing was ensured not to exceed 10 minutes or the material will become rubbery.

4. CURING

Closed flask, which was polypropylene mold with lid cover, was submerged in a water bath at 72°C ± 1°C for 9 hours, followed by half an hour in boiling water. A periodic check of water bath temperature with an accurate thermometer was kept.

5. COOLING

The mold was bench cooled at room temperature for 30 minutes. Then it was immersed in cool water at 15-26°C for 15 minutes before deflasking.

6. FINISHING AND POLISHING

The denture was cut and shaped according to the dimensions required by each test.

FIGURE 2.5 Example of denture base resin, after curing and ready for sorption test.

2.6 Characterization of copolymers, homopolymer and commercial denture base polymer

2.6.1 Fourier Transform Infrared (FTIR) and FTIR-ATR (Attenuated Total Reflectance) analysis

FTIR analysis was done using FTIR Spectrum RX series (PerkinElmer, USA) at 4 scans, from 4000 to 600 cm^{-1} using $2cm^{-1}$ resolution. FTIR-ATR analysis was done using FT-IR Spotlight 400 (PerkinElmer, USA) at the same wavelength and resolution. FTIR-ATR was used for samples that did not dissolved in solvents.

For FTIR analysis, sample was prepared by dissolving it in small amount of toluene, and was cast directly on a sodium chloride (NaCl) cell. The solvent was evaporated off by blowing hot air. Subsequently, the FTIR analysis was performed on each copolymer, homopolymer and macromer.

For FTIR-ATR analysis, the homopolymers and copolymers (solid form) were directly placed on the diamond sample holder and pressure was applied until a beautiful peak with good transmittance appeared.

2.6.2 Thermal analysis

2.6.2.1 Thermogravimetric Analysis (TGA)

A thermogravimetric analyzer (Pyris 6, PerkinElmer, USA) was employed to perform the analysis on each sample. This analysis was intended to analyze the thermal degradation of copolymers and homopolymers and to see thermal stability of FA35 macromer.

About 8-12 mg of the sample was placed into the sample crucible that was inside the furnace of the analyzer. The test was conducted at temperature ranging from 50°C to 900°C at a heating rate of 20°C/min, under nitrogen atmosphere. Plots of weight percentage loss versus temperature were plotted.

2.6.2.2 Differential Scanning Calorimetry (DSC)

Diamond Differential Thermal Analyser (DTA) (PerkinElmer,USA) was used to measure the glass transition temperature (T_g) of macromer, homopolymers, copolymers and commercial denture base resin. Approximately 5-12 mg of each sample was weighed using a microbalance (Mettler, M15) and was placed into an aluminum pan. The sampling aluminium pan was placed into the sample chamber inside the furnace, together with a blank aluminium pan as reference. DSC measurement was conducted at temperature range from 35°C to 200°C or 250°C at heating rate of 20°C/ min.

2.7 Physical properties of copolymers as dental material

2.7.1 Water sorption and water solubility

2.7.1.1 Materials and apparatus

This test required freshly dried silica gel which has been dried at 110°C for at least 1 hour, distilled water, a rack to place the specimens in the dessicator, 2 desiccators, drying oven, tweezers, clean dry towel and dial caliper.

2.7.1.2 Preparations of test specimens

Solid specimens were produced as a thin plate with dimension of (145 mm x 86 mm x 10 mm) and (85 mm x 60 mm x 10 mm). Test pieces were prepared by cutting these plates with mechanical cutter to a round-shaped disc with diameter of 55 mm and 3-4 mm thick. Six discs were cut, grinded and polished with grinding and polishing machine (Buehler, Germany) until they reached the nominal size desired (50 mm diameter with 3-4 mm thickness) as shown in Figure 2.6.

FIGURE 2.6 Example of samples that is ready for sorption test.

Specimens were placed on a rack, inside one desiccator that contained freshly dried silica gel. The desiccator was stored in the oven at 37(±1)°C for 23(±1) h and then it was removed from the oven.

The specimens from the rack were transferred directly to the second desiccator which has been supplied with freshly dried silica gel. The second desiccator was kept at 23(±2)°C. After 60(±10) min in the second desiccator, the specimens were weighed using analytical balance (Denver Instrument Co., USA).

The specimens were weighed to an accuracy of 0.1 mg. The desiccator was kept closed, and opened for the shortest possible period required for removing and replacing specimens. After all the specimens have been weighed, the silica gel in the first desiccator was replaced with freshly dried gel and the desiccator was placed in the oven.

The cycle described was repeated until a constant mass, m_1, to be called the ‘conditioned mass’ was reached, i.e. until the loss in mass of each specimen was not more than 0.2 mg between successive weighings. At this point the volume of each specimen was calculated, using the mean of three diameter measurements and the mean of five thickness measurements. The thickness measurements were taken in the centre and at four equally spaced locations around the circumference.

The conditioned specimens were immersed in water at 37(±1)°C for 7 days (±2 h). After this time, the discs were removed from the water with forceps, wiped with a clean dry towel until free from visible moisture, waved in the air for

15(±1) s and weighed 60(±10) s after removal from the water. This mass was recorded as m_2.

After this weighing, the specimens were reconditioned to a constant mass in the desiccators as described above. The mass of the reconditioned specimens was recorded as m_3.

2.8 Mechanical properties

2.8.1 Flexural strength and flexural modulus

2.8.1.1 Materials and apparatus

This test follows ISO 1567: 1999 specification with slight modifications. The test requires two specimen plates, cutting device for sectioning the plate, standard metallographic grinding papers of range P120 to P200 FEPA (or of 100 to 220 grit), dial caliper, water container (for pre-test conditioning of the strips at 37(±1)°C) and a testing machine calibrated to provide a constant crosshead speed of 5(±1) mm/min. Flexural test rig of the machine consisted of a central loading plunger and two polished cylindrical supports. The supports were parallel and perpendicular to the longitudinal centerline. The distance between centers of the supports was 50(±0.1) mm, and the loading plunger was midway between the supports to within 0.1 mm.

2.8.1.2 Procedure

Ten specimen strips of approximately 65 mm long, 10.5 mm wide and 3.5 mm in thickness were prepared by cutting the specimen plate using Diamond Precision Sawing Machine (Buehler, Germany). All faces and edges of the strips were wet-grinded, smoothened and flattened with the metallographic grinding papers to the required length, width and thickness which was 64 mm x 10.0 (±0.2) mm x 3.3 (±0.2) mm. The measurements of the specimen thickness were made along the long axis with an accuracy of ± 0.01 mm. The specimens were ensured flat-shaped (Figure 2.10).

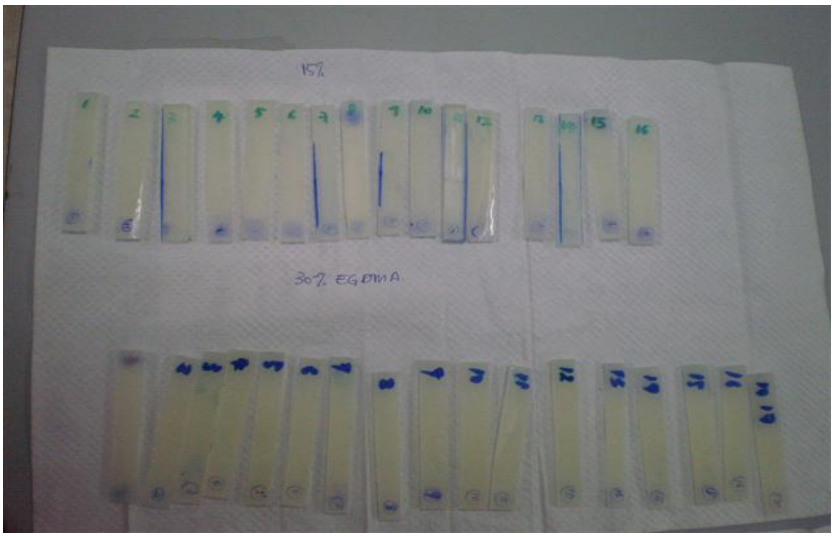


FIGURE 2.7 Example of samples ready for three-point-bend test.

All test specimens prepared were visually inspected to ensure no voids observed. They were stored in water at a temperature of 37(±1)°C for 50 (±2) hours prior to flexural testing. The specimen was taken out from water storage and was placed immediately on the supports of the flexural test rig. The force on the loading plunger was increased, uniformly, using a constant crosshead speed of 5(±1) mm/min until the specimen broke. This test was performed at room temperature of 23- 25°C.

FIGURE 2.8 A three-point-bend test in progress.

2.8.2 Impact strength (Notched - Charpy method) – ISO 1567 :1999

2.8.2.1 Materials and apparatus

This test also requires cutting device for sectioning the specimen plates, standard metallographic grinding papers of progressively finer grades using a grain size of approximately 26 μm (600 FEPA) for the final finishing stage, a dial caliper accurate to 0.01 mm, water container for storing the specimen strips at 23(±1)°C and 37(±1)°C for pre-test conditioning and a pendulum impact testing machine, conforming to ISO 179:1993.

2.8.2.2 Procedure

All faces and edges of the specimens were wet-grinded, smoothed and flattened with the metallographic grinding papers to the required width and thickness. Ten specimen strips of size of 50 mm long, 6 (± 0.2) mm wide and 4 (±0.2) mm in height were prepared. The measurements of the specimen height were made along the long axis with an accuracy of ± 0.01 mm.

A notch (Type A) was cut in the middle of each specimen strip as described in ISO 179:1993, using a motorized notch cutter (RayRan, UK). The notch was cut edgewise to a depth of 1.2 (± 0.1) mm leaving a residual depth beneath the notch of 4.8 (± 0.1) mm approximately. The radius of the notch base (tip) was more or less 0.25 (± 0.05) mm.

The height of each specimen strip near the notch, h, [nominal 4 (± 0.2) mm] and the residual depth, b, [nominal 4.8 (± 0.1) mm] beneath the notch was measured and recorded using a micrometer. Only the specimen strips which are of good quality and fall within the correct size range were used.

FIGURE 2.9 Example of samples ready for impact strength test.

Ten selected specimens were stored in a water container at 37(±1)°C for 7 days (±2 hours). They were conditioned in the water container at 23(±2)°C for 60 (±15) minutes prior to testing. After conditioning, a specimen was removed from the water and was placed on the specimen support of the pendulum impact testing machine. The specimen supports was set at a separation of 40.0 (±0.2) mm.

The specimen strip was placed with the notch facing away from the point of impact of the pendulum. It was placed at the center with regard to the position of the notch and the point of impact of the pendulum. The pendulum was released immediately after removing each of the specimens from the water bath in order to fracture them.

The impact strength value was obtained directly from the machine by keying in the depth and height values of each specimen prior to sample loading and swinging the pendulum. The impact pendulum energy used was 5.42 J with 3.46 m/sec of hammer velocity.

2.9 Statistical analysis

Statistical analysis was made using the SPSS statistical software program (Version 12.0, SPSS Inc., Chicago). The group of materials which underwent water sorption, solubility, impact and flexural tests were analyzed using SPSS.

After data collection, mean values and standard deviations were calculated. Subsequently, means were analyzed with One-way analysis of variance (ANOVA) at the 95% confidence level, to examine variable effects. When significant effects were detected, the post-hoc Scheffé's multiple range tests will be used to determine which group means were different.

2.9.1 Standard deviation (S.D.)

Standard deviation is a basic measure of variability and can be defined as the average of individual scores from the mean. Low S.D. values indicated small variation of values around the mean.

2.9.2 Analysis of variance (ANOVA)

ANOVA is the test of difference between the means. The test analyses whether the difference in the mean values is a true difference or due to a chance. The 'p' values for ANOVA were calculated using the SPSS software. If 'p' value was less than 0.05 ($p<0.05$), it means there were significant differences among the materials. If 'p' value was higher than 0.05, it means there were no significant differences between the materials.

2.9.3 Scheffé's test

Post-hoc analysis (Scheffé's) test was carried out if there were significant differences amongst the group from the ANOVA test ($p>0.05$). Scheffé's

confidence interval value (I) was calculated and then compared with the mean difference between any two groups separately. If the (I) value was more than the differences between the two means, the differences were considered not significant and vice versa.

2.10 Morphology study

2.10.1 Digital microscopy analysis

Visual inspection was made to observe the type of fracture in the copolymers resulting from the flexural test. First, analysis was performed by visual inspection of the fractured surfaces using a digital microscope (Dinolite Digital Microscope, Taiwan) at 70 and 200 times magnifications. Fragments of each specimen were referred to as fragment A (FA) and fragment B (FB).

2.10.2 Scanning Electron Microscopy (SEM) analysis

One fragment of the fractured surfaced was cut into smaller pieces (approximately 8 mm x 8 mm x 3 mm), by not affecting the fractured surface. The samples were then mounted on aluminum stubs, sputter coated with gold (Polaron SC7640 sputter coater; Thermo VG Scientific, United Kingdom), and observed with a Phillips XL series SEM (LabX, Midland, ON, Canada). The entire surface of the sample was examined, and images that were representative of the sample were taken. Images of each copolymer were analyzed and compared with the controls.

FIGURE 2.10 Specimens on the holder after coating.

CHAPTER 3

RESULT AND DISCUSSION

3.1 Characterization of FA35 macromer

3.1.1 Acidity

Acidity is a measure of the amount of free fatty acids present in oil. It is determined by titrating a known weight of oil with standardized sodium hydroxide (KOH) solution. It is expressed as acid value or acid number, AN, which is the number (mg) if KOH used to neutralize the free acids in 1 gram of oil sample. AN, is calculated as shown in section 2.3.1.

The KOH solution used for this measurement was standardized by titration using potassium hydrogen phthalate (KHP) as shown in section 2.3.1. A small amount of KHP with 50 mL water was titrated with 0.08 N of KOH solution until the first appearance of a permanent pink color. Titration was done using 1% w/v phenolphthalein indicator. The average normality of KOH shown in Table 3.1 is 0.08N.

Table 3.1
Standardization of 0.1 N KOH ethanolic solutions with KHP.

Titration	1	2
Weight of KHP, g	0.4423	0.4467
Volume of KOH used, mL	28.25	28.15
Normality of KOH, N	0.0767	0.0769
Normality	0.08 ± 0.00	

Table 3.2 shows average acid number of FA35 macromer which is 45.17 (±0.11) mg KOH/g macromer. This value indicated that the macromer consists of medium value of free fatty acids.

Table 3.2
Acid number of FA35 macromer.

Titration	1	2	Control, V_b
Weight of macromer, W_s /g	0.5494	0.5284	-
Volume of KOH used to titrate sample, V / mL	5.90	5.70	0.15
Normality, N	0.0768	0.0768	-
AN, mg KOH/g macromer	45.0924	45.2537	-
Average AN	45.17± 0.11 mg KOH/g macromer		-

3.1.2 Iodine value (Wijs method)

The iodine value is a measure of the unsaturation of fats and oils. It is expressed as the number of grams of iodine absorbed by 100 g of the oil under the test conditions. Wijs method was done using a back-titration technique. Iodine value, IV is calculated as follows:

IV, g iodine/100g alkyd = 12.69 N (V_b-V_s) / W,

where N : normality of sodium thiosulphate ($Na_2S_2O_3$) used (N)

V_b : volume of $Na_2S_2O_3$ solution used for blank test (mL)

V_s : volume of $Na_2S_2O_3$ solution used for sample determination (mL)

W : weight of macromer of the test portion (g)

12.69 : equivalent weight of $Na_2S_2O_3.5H_2O$

The $Na_2S_2O_3$ solution used in this measurement was standardized using potassium dichromate ($K_2Cr_2O_7$) solution. The procedure is as shown below:

To prepare a standard $K_2Cr_2O_7$ 0.1N solution, dried 1.2290 g of $K_2Cr_2O_7$ was used.

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

$$Cr_2O_7^{2-} + 6S_2O_3^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

The equivalent weight of $K_2Cr_2O_7$ = 294.2 / 6 = 49.03

No. equivalent of $K_2Cr_2O_7$ = 1.2290 / 49.03

= 0.02507 mol

Therefore, normality of $K_2Cr_2O_7$

= No. equivalent of $K_2Cr_2O_7$ / V solution (L)

= 0.02507 mol / 0.25 L

= 0.10028 mol/L @ **0.10028 N.**

Then, the 0.10028 N $K_2Cr_2O_7$ solution was titrated with $Na_2S_2O_3$ solution.

Table 3.3
Standardization of thiosulphate solution using 0.10028 N dichromate solutions.

Titration	**1**	**2**
Volume of thiosulphate used, mL	22.00	22.50
Normality of thiosulphate, N	0.1140	0.1114
Average normality of thiosulphate, N	0.11± 0.00	

Therefore, normality of $Na_2S_2O_3$ was 0.11 (± 0.00) N. Thiosulphate solution was then used to titrate the macromer sample in Wijs reagent and its control.

Table 3.4
Iodine value of the FA35 macromer**.**

Titration	Sample, V_s1	Sample, V_s2
Weight of macromer, g	0.5199	0.5402
Volume of thiosulphate used, mL	41.60	41.95
Iodine value, IV (I_2/100g alkyd)	10.2606	8.9484
Average IV	9.60 ± 0.93 g I_2/100g macromer	

Blank, V_b1 = 44.90 mL; Blank, V_b2 = 45.76 mL. Therefore, V_b, average volume of titration for controls (blank) = 45.33mL

The IV of this macromer, as shown in Table 3.4 has a value of 9.60 (± 0.93) iodine per 100 g macromer. This very low IV value placed FA35 macromer in the non-drying alkyd category (Guner et al., 2006). The low IV also indicated low amount of unsaturation of fats and oils contained in this macromer. This unsaturation is used to copolymerize with MMA to produce a new copolymer.

3.1.3 Relative density @ specific gravity

The relative density (specific gravity) is the ratio of the mass of a given volume of material to the mass of water of the same volume at *t*°C and is expressed as follows:

The specific gravity at t°C is:

$$\frac{W_s - W_b}{(W_w - W_b) - [1 + 0.000025\,(t - 30)]},$$

where W_s : weight of the macromer and bottle (g)

W_b : weight of empty bottle (g)

W_w : weight of water and bottle (g)

t : ambient temperature

0.000025 : coefficient of glass expansion

From Table 3.5, relative density of FA35 macromer towards water at 30°C was 1.07±0.00.

Table 3.5
Specific gravity of FA35 macromer.

Weight/g	Sample 1	Sample 2
W_s	89.3299	87.6283
W_b	37.3078	35.4691
W_w	86.8399	85.1260
Specific gravity	1.0719	1.0720
Average specific gravity	1.07±0.00	

3.1.4 Volatile matter content (Porim test method)

The volatile matter is defined as the loss in weight of the oil when heated under the test condition specified. The volatile matter is expressed as percentage by weight using the following formula as follows:

$$\% \text{ volatile matter} = [W_b - W_d / W_b - W] \times 100,$$

where W : weight of dish (g)

W_b : weight of dish and oil (g)

W_d : weight of dish and oil after drying (g)

Table 3.6
Volatile matter content of FA35 macromer.

Item	Weight/g		
	Dish 1	Dish 2	Dish 3
W, empty dish	18.6950	18.1625	18.8567
W_b , dish + macromer	28.7365	28.9427	28.9930
W_d , dish + macromer, heated and cooled	28.7102	28.9147	28.9623
Volatile matter, %	0.2619	0.2597	0.3029
Average volatile matter, %		0.27 ± 0.02	

The volatile matter is defined as the loss in weight of oven-heated macromer at 103°C for exactly 2.5 hours. Table 3.6 shows FA35 macromer

contains of 0.27 (±0.02) % volatile matters. The result shows that this macromer has low moisture content and has long shelf-life (Akintayo and Bayer, 2002)

3.1.5 Summary of the physico-chemical characteristics of FA35 macromer from palm oil

The physico-chemical characteristics of the palm oil based macromer as discussed in the preceding sections are summarized in Table 3.7.

Table 3.7
Physico-chemical properties of the FA35 macromer.

Property	Value
Color	Light clear yellowish
Acid number	45.17 mg KOH/g macromer
Iodine value	9.60 g iodine /100 g macromer
Relative density	1.07
Volatile matter content	0.27%

Values are mean of standard deviation of replicate determination

In common oils, general properties of the oil depend on the nature of fatty acids and the proportions in which they are present. One of the most dominant parameter affecting oil properties is the degree of unsaturation. This non-drying alkyd was used as a starting material for preparation of copolymer with MMA in the following sections.

3.2 Copolymerization and conversion

In this copolymerization process, the structure of macromer has un-conjugated double bond that could copolymerize with MMA. Four parameters of this copolymerization reaction were studied, namely monomer concentration, initiator concentration, reaction time and temperature.

Table 3.8
Yield of solution copolymerization of macromer and MMA at 80°C - S series.

Sample	Macromer /g	MMA /g	Toluene/ g	BPO /g	Macromer: MMA	Reaction time/ h:min	Yield /%
S1	20	20	40	2(2.4%)	1.00	5:35	45.6
S2	20	20	20	4(6.3%)	1.00	5:40	39.2
S3	20	20	30	2(2.8%)	1.00	5:35	35.2
S4	20	20	30	2(2.8%)	1.00	5:05	48.8
S5	20	30	20	2(2.8%)	0.67	1:05	35.5
S6	20	30	30	2(2.4%)	0.67	2:15	48.5
S7	20	30	30	2(2.4%)	0.67	4:05	48.0
S8	20	40	30	2(2.2%)	0.50	0:35	65.0
S9	20	40	40	2(2.0%)	0.50	3:40	55.0
S10	20	40	40	2(2.0%)	0.50	3:25	57.5
S11	20	40	50	4(3.5%)	0.50	6:55	56.9
S12	20	40	40	4(3.8%)	0.50	4:30	70.5
S13	20	45	40	2(1.9%)	0.44	6:00	75.0
S14	20	45	40	2(1.9%)	0.44	5:00	62.1
S15	20	45	40	4(3.7%)	0.44	5:00	70.3
S16	20	45	40	4(3.7%)	0.44	2:05	57.9
S17	20	45	30	2(2.1%)	0.44	4:35	96.4
S18	20	45	30	2(2.1%)	0.44	1:05	92.8
S19	20	45	30	4(4.0%)	0.44	0:40	54.1
S20	20	45	30	4(4.0%)	0.44	0:30	64.1

Item colored yellow indicated that the initiator with solvent was added half the amount (g) prior mixing and the other half was after 1-2 hours of mixing.

For each copolymerization (solution and bulk), yield of copolymerization reaction was calculated as follows:

(*Weight of copolymer obtained / initial weight of monomers mixture) x 100%*

3.2.1 Analysis of the solution polymerization method

Table 3.8 summarizes the results of 20 copolymerizations using toluene as solvent. In general, yield of reaction increases with increasing amount of MMA monomer. This trend can be seen from Sample 1 to Sample 12, MMA amount has been increased from approximately 35% to 70%, and the yield of copolymerization increased from 29% to 70%.

Effect of initiator addition to copolymerization

In cases of sample 13 to sample 20, the amount of monomers (macromer and MMA) and solvent was fixed. Increase of BPO addition from 2% to 4% decreased the yield from 75% to 70% (for sample S13 and S15) and from 62% to 57% (for sample S14 and S16).

In most cases (indicated with black line), it is observed that the addition of total amount of initiator prior to mixing gave more yields compared to samples whose initiator was added half prior to mixing and the other half later in the middle of reaction. For example in sample S13 (all initiator added prior mixing), it gave 75% yield while sample S14 gave only 62% yield. About 70% yield was obtained from sample S15 compared to 57% from sample S16. Addition of initiator at once produced more yield of the copolymer. However, this trend is not observed in samples 3 & 4, samples 9 & 10 and samples 19 & 20 (indicated with

red lines). The yield of copolymers corresponds to the amount of initiator that initiates the radical polymerization plus the thermal polymerization. BPO starts to react at 70°C and will finally degrade at increasing temperature therefore will stop the polymerization. Further prolong of reaction time did not increase the copolymer yield as observed in samples 3 & 4 and samples 6 & 7. Sample S17 gave most yields, which was about 96% w/w.

Effect of solvent on copolymerization

The experiments in the S series suggest that solution copolymerization of macromer and MMA could be conveniently conducted at 80°C because we got 96% yield for the copolymerization and this result is reproducible. However, solvent addition must be added sufficiently to prevent mixture from gelling up due to rapid increase in viscosity. S series used 30 to 48 wt% of toluene solvent and was from 1:0 to 2:17 in most of reactant to solvent ratios.

This solvent copolymerization method was successfully done using about 30-50% of solvent, 18-31% of macromer and approximately 24-46% of MMA. Initiator with solvent (2-6 w/w %) was added prior to the reaction.

3.2.2 Effect of monomer concentration to conversion

The series of J and L were formulated with the same amount of solvent and initiator. As shown in Figure 3.1, both series shows an increment in yield when the MMA is increased.

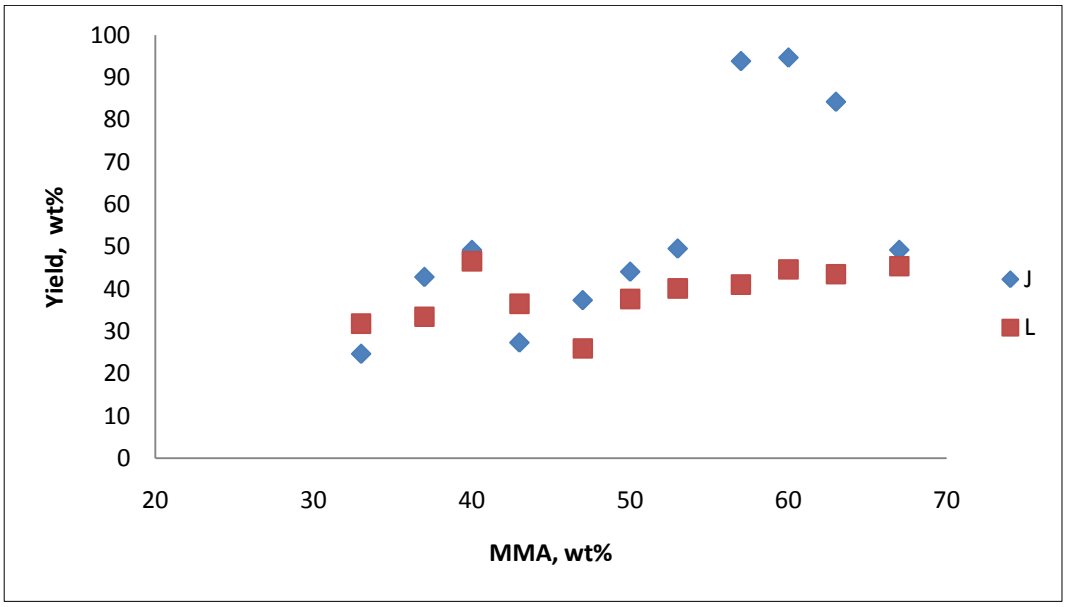


FIGURE 3.1 Yield of Series J and L of solution copolymerizations corresponding to increasing amount of MMA.

Figure 3.2 demonstrates a different observation in the yield trend. Increase of macromer from 5% to 20 % increases the yield of macromer-MMA polymerization, both for bulk A and bulk B series. Further increase to 30% of macromer does not produce much difference in the yields for bulk B but shows a decrease in bulk A. Increase trend in bulk B may result from the effect of cross-linker that increases the polymerization of MMA while it is copolymerizing with macromer, giving more yield in the end. On the other hand, the homopolymerization of MMA produces moderate yield which is about 55%.

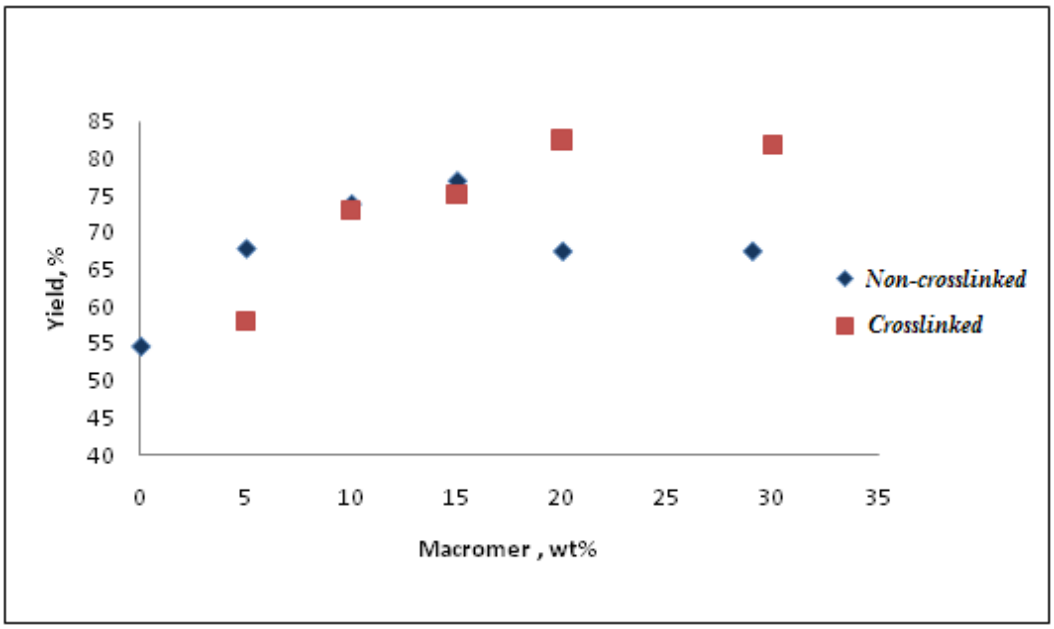


FIGURE 3.2 Yield of series Bulk A and Bulk B corresponding to increasing amount of macromer.

3.2.3 Effect of temperature to conversion

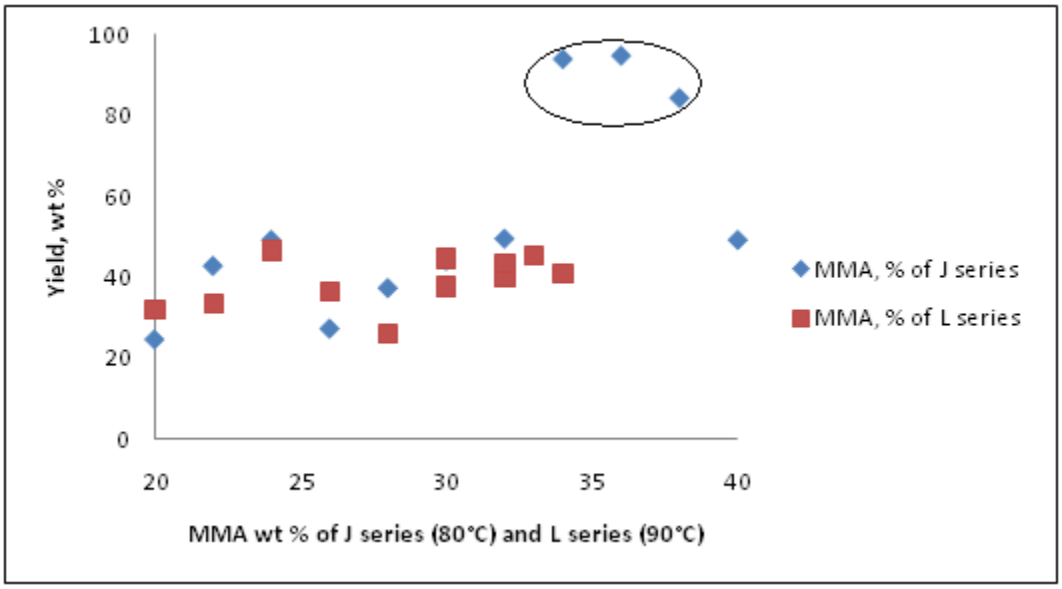


FIGURE 3.3 Yield of series J and L corresponding to increasing temperature of 80°C to 90°C.

It is well known that the rate of the initiation and propagation reactions generally increases with rising in temperature; therefore the yield of polymer should increase with the rise of polymerization temperature (Ohtani et al., 1989). In this study, only two different temperatures were investigated, 80°C and 90°C.

PMMA normally has T_g of 100-110°C (depending on its tacticity) and the MMA monomer has boiling point of approximately 101°C. Figure 3.3 shows no significant difference in yield percentage in the series of 80°C and 90°C. However, samples J8, J9 and J10 (contained 34 to 38 MMA wt %) which were conducted at 80°C, produce significantly higher yield compared to the samples of L series respectively. This observation defies the fact that higher temperature would give higher yield, presumably due to the faster decay of radical at 90°C.

3.3 Characterization of copolymer, homopolymer and commercial denture base polymer

3.3.1 FTIR/ATR analysis

The spectra of the copolymers are compared with the macromer and PMMA spectra as shown in Figure 3.4. The assignment of major peaks of FA35 macromer and PMMA are listed in Table 3.9 and Table 3.10.

Table 3.9
Major peaks assignment of FA35 macromer.

Wavenumber (cm^{-1})	Bonding
744	Aromatic C-H bending
1072-1378	Strong and broad C-O stretching
1580, 1600	Breathing mode of aromatic ring
1731	Very strong C=O stretching
2854, 2925	Very strong C-H stretching
3440	O-H stretching

Table 3.10
Major peaks assignment of PMMA.

Wavenumber (cm^{-1})	Bonding
694,729	1,1-disubstituted out of plane
1148,1242	C-O stretching
1615	Conjugation of C=C
1731	Conjugation of C=O stretching
2940,3033	Strong =C-H stretching

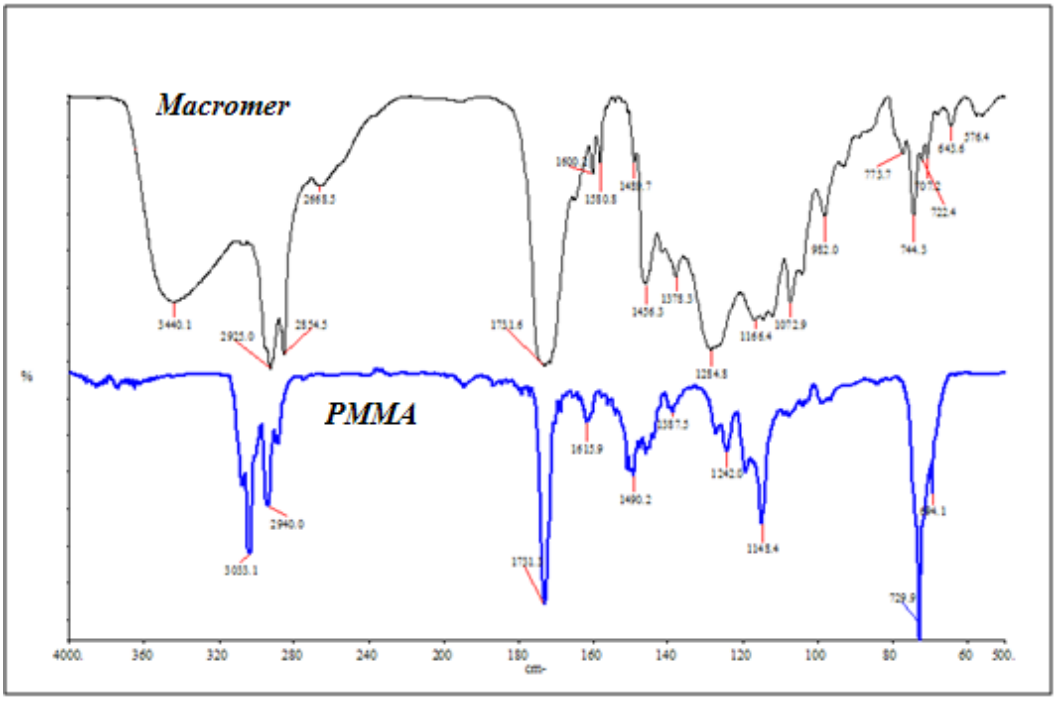


FIGURE 3.4 Characteristic peaks of FA35 macromer and PMMA.

Figure 3.4 shows characteristic peaks of palm oil-based macromer and PMMA polymer. Macromer has broad hydroxyl peak at 3440 cm^{-1} while PMMA has strong =C-H stretching 2940 cm^{-1} and 3033 cm^{-1}. Both macromer and PMMA has strong conjugation carbonyl bond observed at 1700 cm^{-1}. The assignments of other major peaks are as listed in Table 3.9 and Table 3.10.

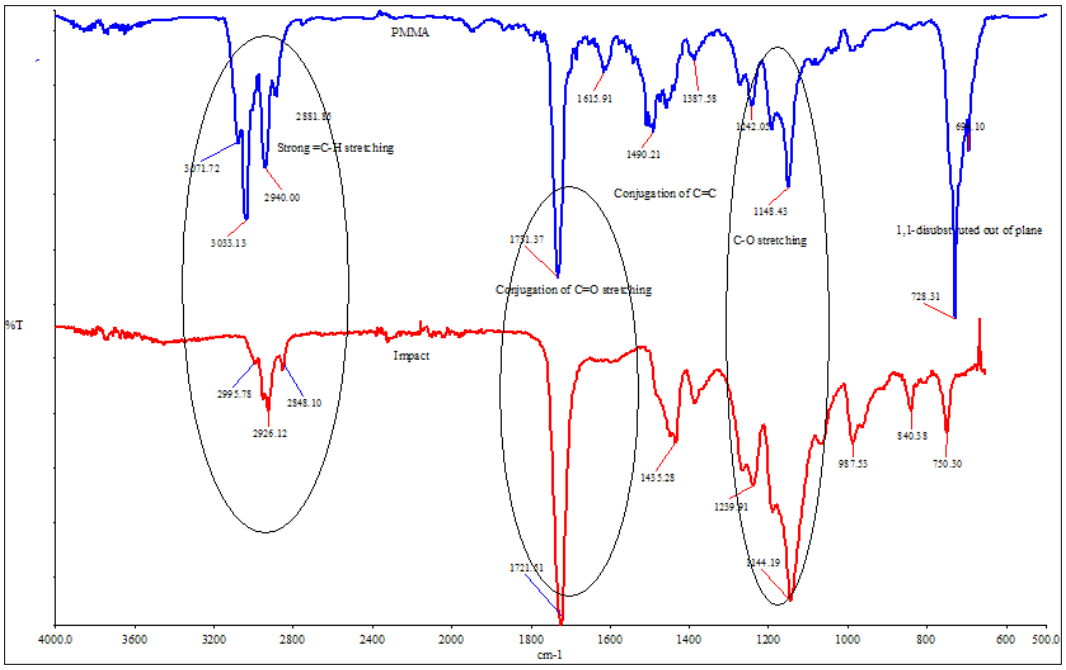


FIGURE 3.5 Spectra of PMMA *(blue)* and commercial denture-base Lucitone 199® *(red)*.

In Figure 3.5, comparison is made between spectra of homopolymer PMMA and Lucitone 199®. It is observed at 2900 cm^{-1} – 3000 cm^{-1} of Lucitone 199® spectra has strong =C-H stretching as in PMMA spectra. Lucitone 199® also has conjugation of carbonyl stretching at 1700 cm^{-1} and C-O stretching at around 1200 cm^{-1} - 1400 cm^{-1} as observed in PMMA. The similarities are shown in circles in Figure 3.5 and it confirms that Lucitone 199® is a PMMA based dental material.

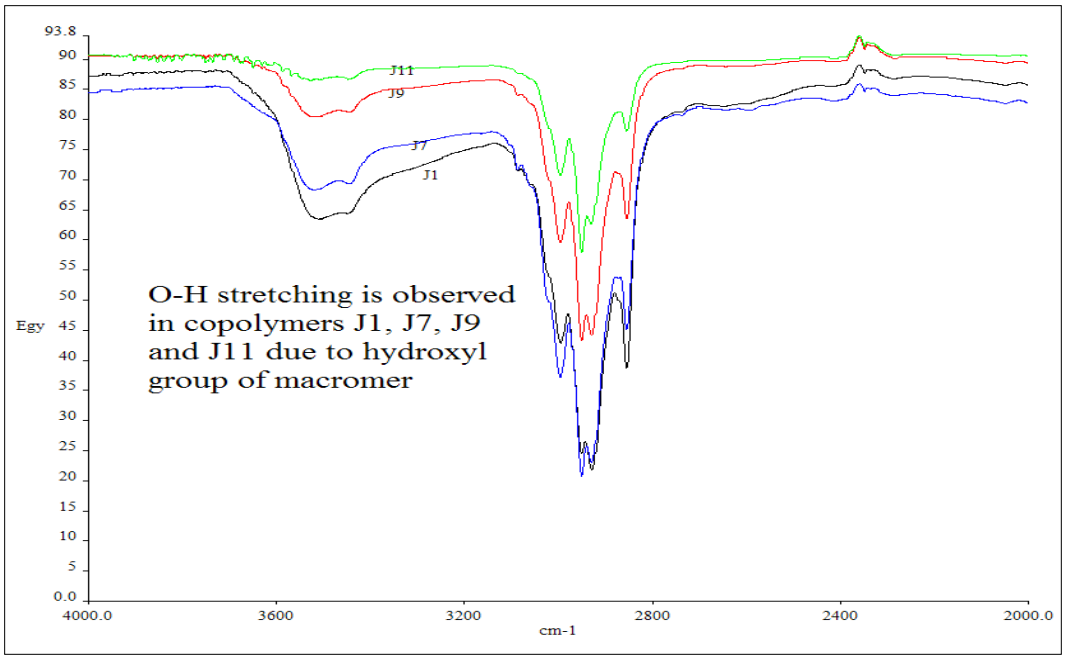


FIGURE 3.6 Spectra of copolymers of J1 *(black)*, J7 *(blue)*, J9 *(red)* and J11 *(green)* from solution copolymerization.

Figure 3.6 shows the spectra of copolymers from solution polymerization namely J1, J7, J9, and J11 having the obvious peak of hydroxyl at ~3400 cm^{-1} as in the macromer. The more the addition of macromer, the more apparent are the peaks in the range of 3500-3600 cm^{-1}. J11 is the copolymer with the least macromer composition and the macromer percentage increases from J11 to J1.

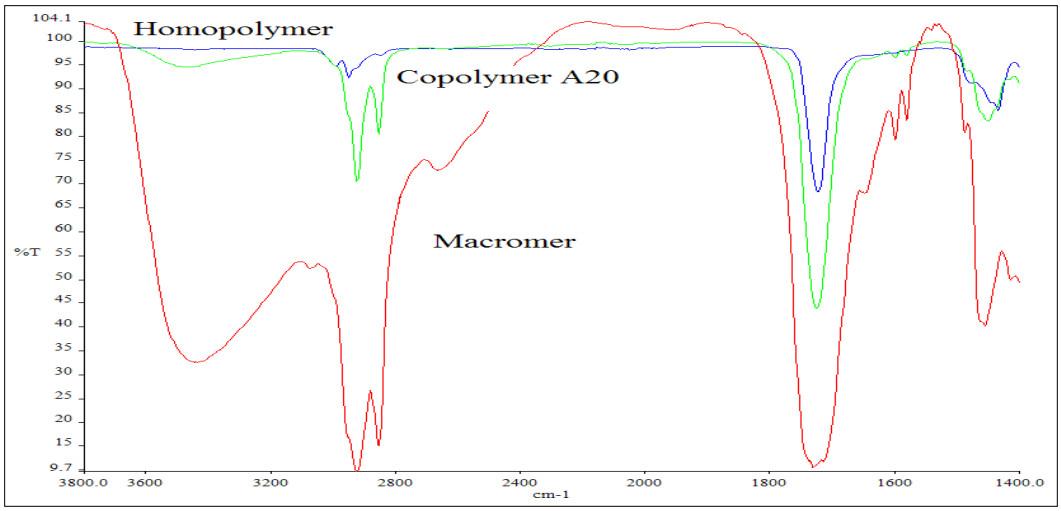


FIGURE 3.7 (a) Comparison of FTIR spectra of non-crosslinked macromer-MMA copolymer (A20) with PMMA alone and unmodified macromer.

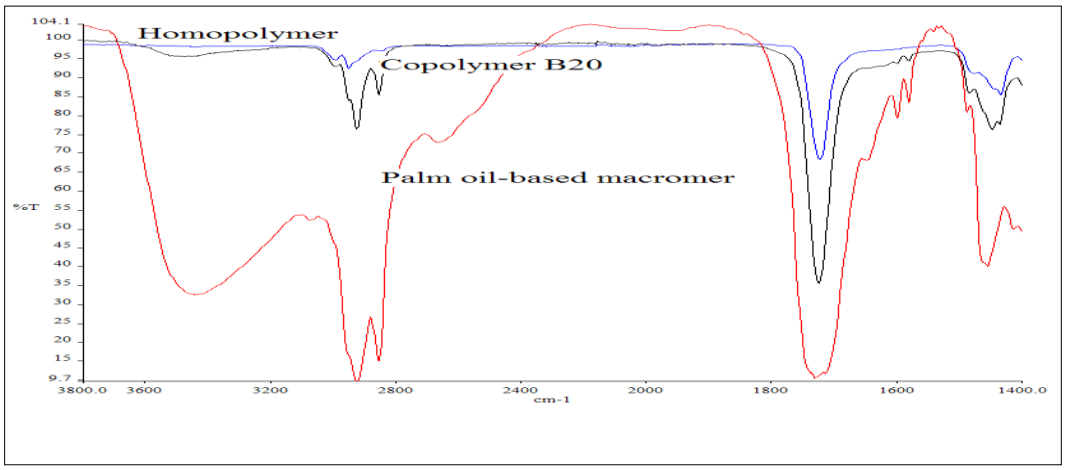


FIGURE 3.7 (b) Comparison of FTIR spectra of crosslinked macromer-MMA copolymer (B20) with PMMA alone and unmodified macromer.

Figure 3.7 (a) and (b) show comparison of FTIR spectra of non-crosslinked and crosslinked macromer-MMA copolymer respectively with PMMA alone and unmodified macromer. The IR stretches at 2900 and 3400 cm^{-1} found in A20 and B20, Figure 3.7 (a) and (b), respectively, confirm the existence of copolymers representing both characteristic peaks from PMMA and macromer.

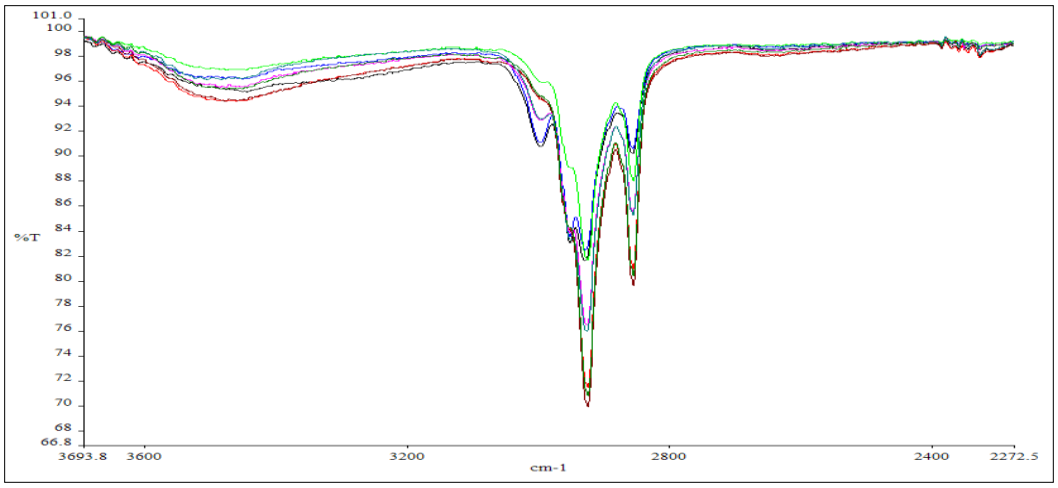


FIGURE 3.8 (a) Comparison of FTIR spectra of all crosslinked and non-crosslinked macromer-MMA copolymer, A10 to A30 and B10 to B30.

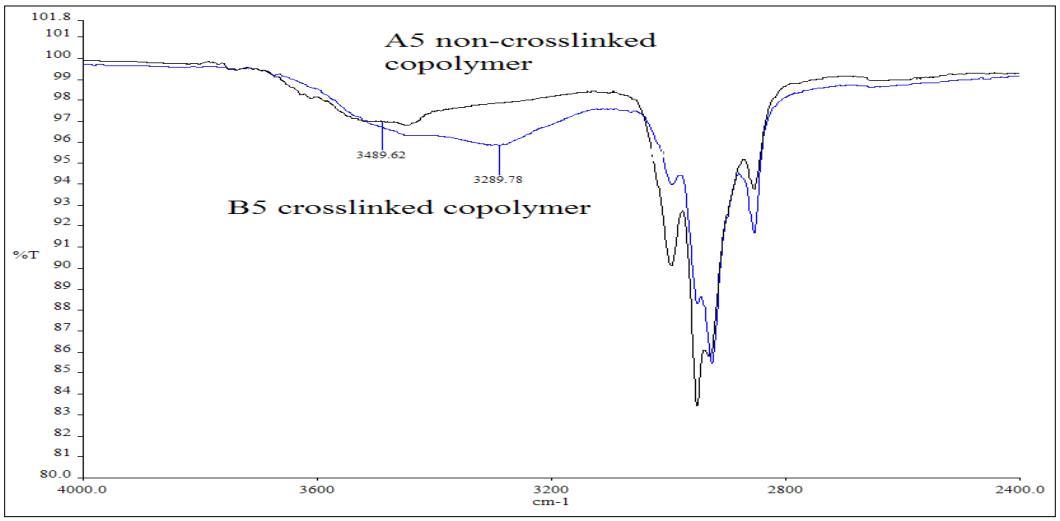


FIGURE 3.8 (b) Comparison of FTIR spectra of non-crosslinked macromer-MMA A5 copolymer *(black)* with its respective cross-linked B5 copolymer *(blue).*

Figure 3.8 (a) shows comparison of FTIR spectra of all crosslinked and non-crosslinked macromer-MMA copolymer, A10 to A30 and B10 to B30. It is clear that all the copolymers have similar characteristic peaks and no apparent difference observed amongst them. This observation explains the non-significant difference observed in mechanical strength of crosslinked and non-crosslinked

copolymers. Exception is only observed in A5 and B5 copolymer as in Figure 3.8 (b) where a very small shift occurred to O-H band which is from 3400 to 3200 cm^{-1}. This small shift also explains the insignificant difference in mechanical or sorption properties of A5 and crosslinked B5.

However, a significant difference is observed when B20 and B30 copolymers exhibit lower sorption values compared to those respective A copolymers (Figure 3.20) notwithstanding the addition of high macromer amount (wt%). This is as hypothesized due to crosslink nature that prohibits further absorption of water into the molecule.

3.3.2 Thermal analysis

Thermal analysis is a group of techniques which study the properties of the sample against temperature change. The technique may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these (Haines, 1995). In this work, two types of thermal analysis was discussed, namely TGA and DSC.

3.3.2.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TG or TGA) is a technique that measures the sample weight as the temperature is changed by means of a programmed rate of heating (Bikales, 1971). A sensitive balance is used to follow the weight change of a sample, as a function of time as the temperature is increased (Seymour and Carraher, 1992).

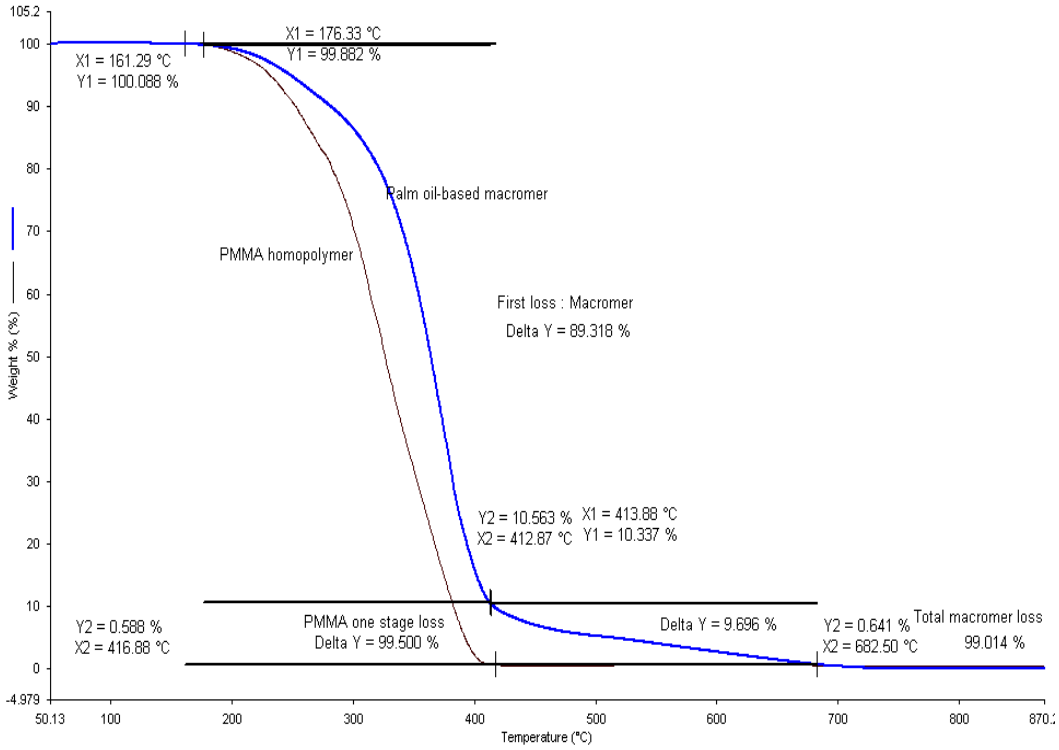


FIGURE 3.9 TGA thermogram of palm oil-based macromer and PMMA homopolymer.

Figure 3.9 shows TGA thermograms of macromer and PMMA homopolymer. PMMA exhibits a single mass loss over a fairly broad temperature range. When heated in nitrogen or inert atmosphere, polymeric materials react by two general routes, often related to their mode of polymerization and the heat of polymerization. They may either depolymerise or carbonize (Haines, 1995). The PMMA homopolymer is stable up to 161°C, and then loses about nearly all of its mass rapidly by 417°C. This suggests that PMMA degrades probably via the unzipping mechanism (depolymerization) to produce complete monomer units as reported for similar poly(methacrylates) bearing the 1,3-dioxolane ring (Ilter et al., 2002, Coskun et al., 1998) and also for poly(methylmethacrylate) (Wang,

1998). Meanwhile, the macromer thermogram shows typical alkyd degradation behavior (Guclu and Orbay, 2009). It shows fairly good thermal resistance to thermal degradation with ~89% and ~100% losses at 414°C and 683°C respectively.

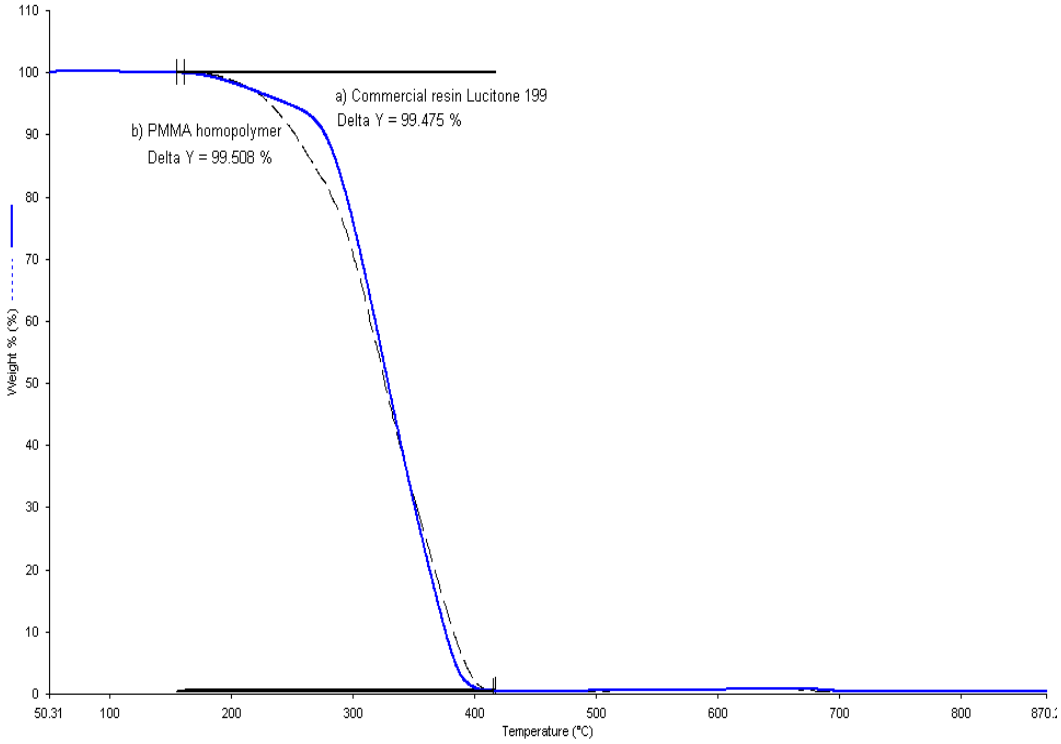


FIGURE 3.10 Comparison of TGA thermograms of a) Commercial Lucitone199® with b) PMMA homopolymer.

Figures 3.10 show commercial Lucitone 199® and experimental PMMA homopolymer TGA thermograms. Both exhibit rapid single mass loss of 99% starting at 160-170°C until 410 – 420°C. These thermal data confirmed that Lucitone 199® was based on PMMA.

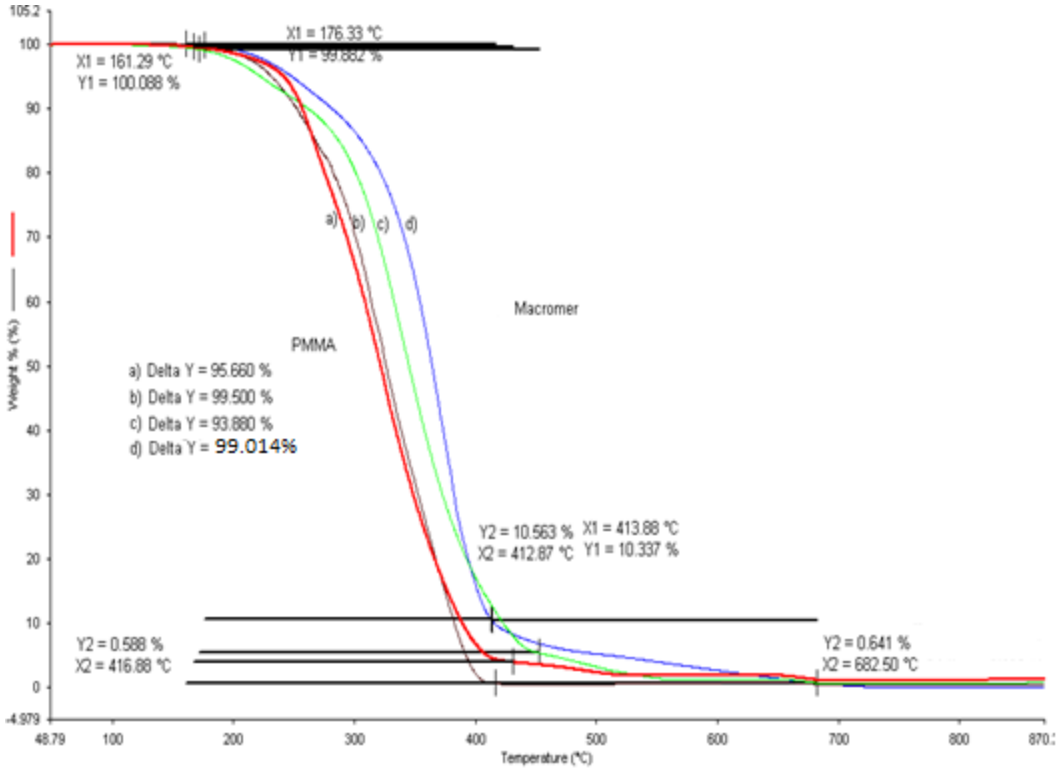


FIGURE 3.11 Comparison of TGA thermograms of a) Non-crosslinked A15 b) PMMA homopolymer c) Crosslinked B15 copolymer d) Macromer.

Figure 3.11 compares PMMA and macromer TGA thermograms with chosen non-crosslinked and crosslinked copolymers thermograms (of 15% incorporation of macromer with MMA). Copolymers A15 and B15 show good thermal stability as they start to degrade rapidly from 160 -170°C until 431-452°C with single weight loss of 96% and 94% respectively. The initial degradation temperature, IDT of crosslinked B15 copolymer (172°C) is higher than the non-crosslinked A15 (167°C). The crosslinked copolymer B15 finished degradation at 20°C higher than the non-crosslinked A15, indicates a better thermal stability.

In general, all crosslinked copolymers show higher value of IDTs and FDTs compared to their respective non-crosslinked copolymers. These values are

summarized in Table 3.11. Figure 3.12 shows TGA thermograms of non-crosslinked A5 and crosslinked B5 that show single stage weight loss of 98% and 97 %. The single stage weight loss is also clearly observed in A10 & B10 (Figure 3.13) and A15 & B15 (Figure 3.11).

Table 3.11
TGA data of macromer, PMMA, commercial Lucitone 199® and macromer-MMA copolymers.

Polymer Code	Stage of wt. loss	IDT (°C)	Temp. at 50% wt. loss (°C)	FDT (°C)
Macromer	1	176	360	682
PMMA	1	161	330	416
Lucitone 199®	1	170	330	420
A5	1	163	313	439
B5	1	228	395	468
A10	1	204	336	451
B10	1	210	356	515
A15	1	167	325	431
B15	1	172	357	452
A20	1	170	338	431
B20	1	172	350	454
A30	1	160	344	431
B30	1	163	369	455

IDT: Initial degradation temperature
FDT: Final degradation temperature

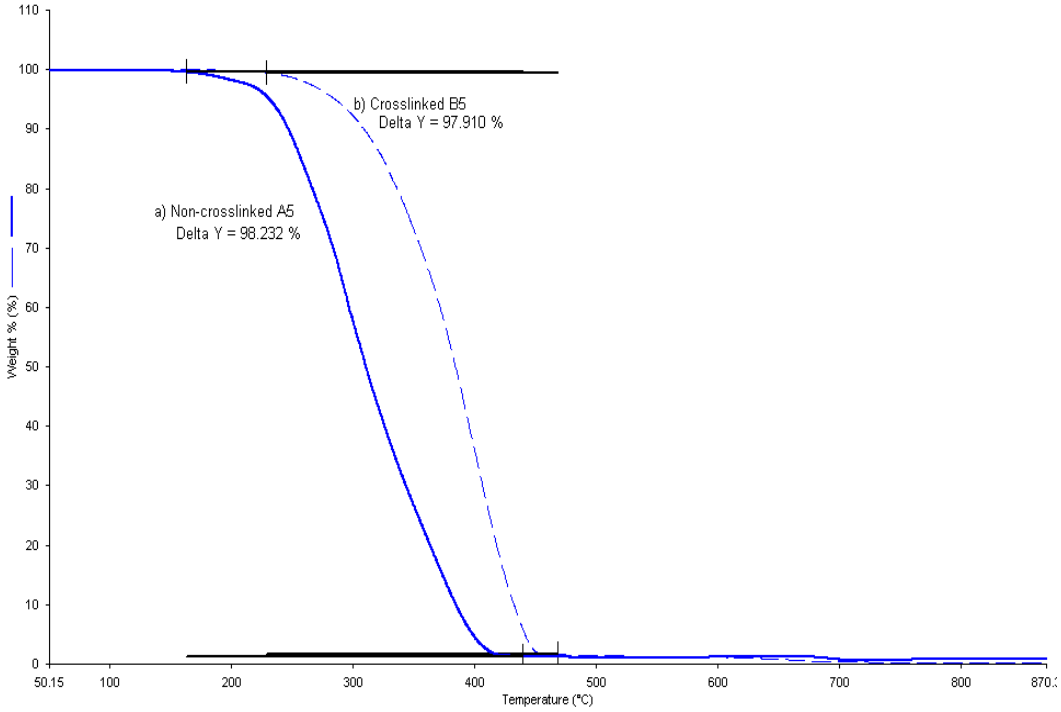


FIGURE 3.12 TGA thermograms of a) non-crosslinked A5 and b) crosslinked B5 copolymers.

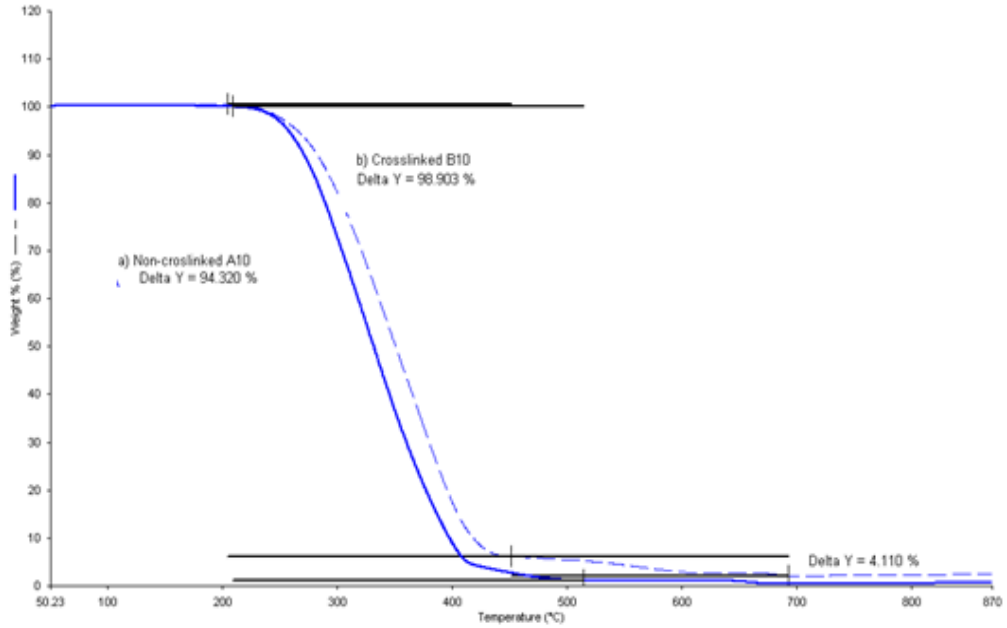


FIGURE 3.13 TGA thermograms of a) non-crosslinked A10 and b) crosslinked B10 copolymers.

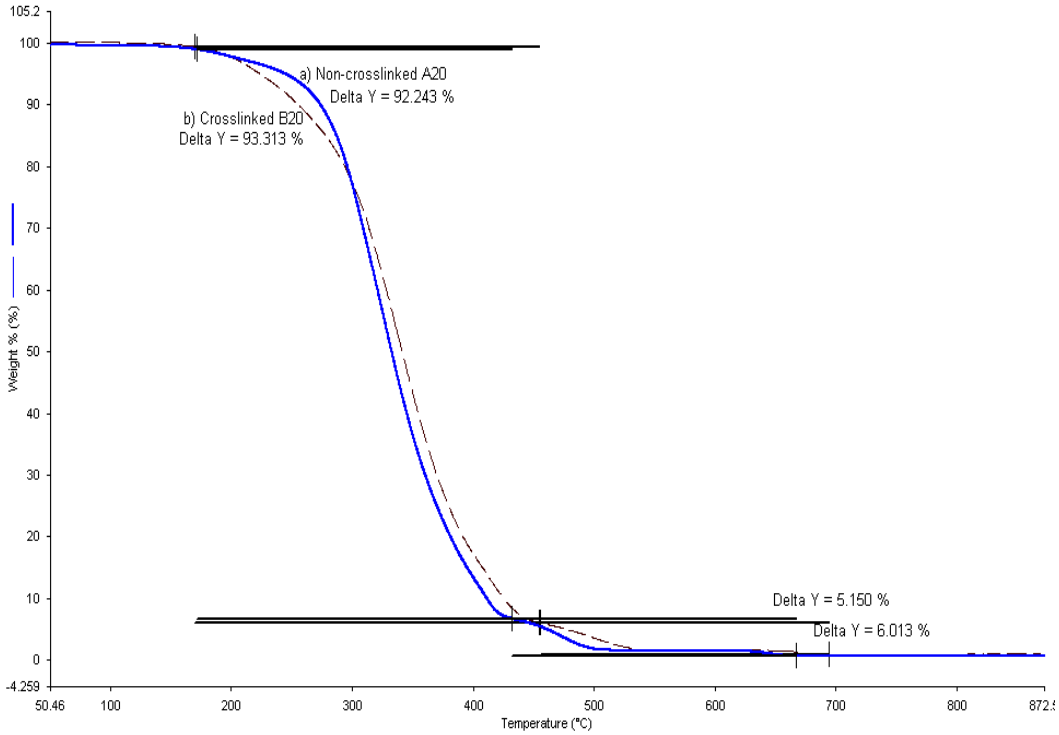


FIGURE 3.14 TGA thermograms of a) non-crosslinked A20 and b) crosslinked B20 copolymers.

In Figure 3.14, A20 is stable up to 170°C and degrades until 431°C with weight loss of 92%. B20 is also stable up to 170°C and degrades until 454°C with 93% weight loss. Beyond 431°C and 454°C ($T_{d,endset}$), activity is probably due to the annealing of carbon residue.

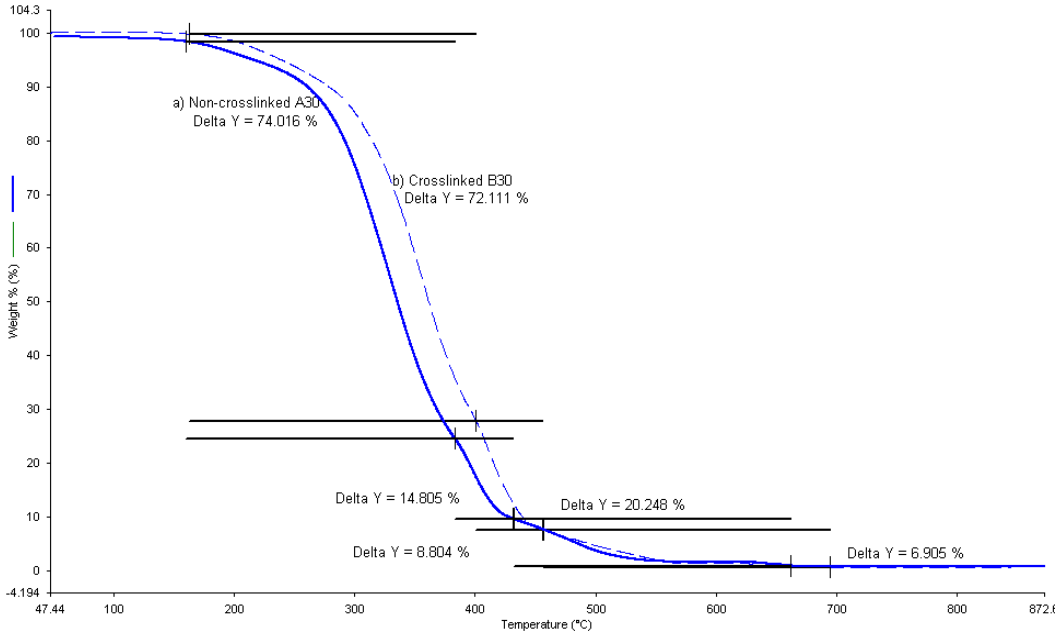


FIGURE 3.15 TGA thermograms of a) non-crosslinked A30 and b) crosslinked B30 copolymers.

Figure 3.15 shows TGA thermograms of A30 and B30 copolymers that starts to degrade at 160°C and 163°C. $T_{d,endset}$ are observed at 431°C and 455°C which denote the temperature where evaporation of the pyrolysis products completes, with total 89% and 92% of weight loss respectively. However, no structural relationship between the thermal stability and the macromer employed could be established. Overall, the crosslinked copolymers have better thermal stability than the non-crosslinked copolymers (Table 3.11).

These thermal data suggest that the maximum curing temperature for these copolymers was 150°C. The IDTs of PMMA and macromer alone were even higher, which was above 161°C and 176°C respectively. Therefore, the curing temperature found appropriate was only 100-120°C the most.

3.3.2.2 Differential Scanning Calorimetry (DSC)

DSC is a technique to determine the thermal transitions of polymeric materials. The DSC thermogram is recorded as the heat differential between the reference material and samples versus temperature (McCabe and Walls, 1998). DSC is used to measure the glass transition temperature (T_g) of the FA35 macromer, homopolymer, copolymers and commercial denture base polymer.

T_g is a temperature at which there is an absorption or release of energy, as the temperature is raised or lowered (Seymour and Carraher, 1992). For an amorphous polymer, it is a hard glass below its T_g and becomes soft and elastic above its T_g (Braun et al., 2001).

Below the T_g, the polymer segments do not have enough energy to rearrange or to rotate themselves. Such material is brittle as glass. As the sample is heated, there is a gradual increase in volume and energy, until at T_g, the chains become more mobile and the polymer become more plastic or rubbery. Further heating, allows the polymer to crystallize and then melts (Haines, 1995).

In the context of denture-base polymers, the determination of the T_g is a very important aspect, in particular, the relationship of T_g to moulding temperature. In order to avoid dimensional changes due to creep, a high value of T_g is advantageous, and a low T_g results in the production of relatively small

internal stresses within heat-curing materials and reflected high residual monomer values (Huggett et al., 1990).

Several factors related to chemical structure affect T_g. Tacticity, the arrangement of substituent on a polymer chain (the orderliness of the succession of configurational repeating units), is particularly important. Isotactic PMMA has a low T_g (approximately 40°C), atactic PMMA has an intermediate T_g (105°C) and syndiotactic has a higher T_g (160°C). Crosslinking also increases the glass transition of a polymer by introducing restrictions on the molecular motions of the chains (Meric and Ruyter, 2007).

A typical value of T_g for a heat curing material in this study is 105°C (McCabe and Walls, 1998). This value is somewhat higher than any temperature which the denture base should reach during 'normal' service. The value of modulus of elasticity decreases and the potential for creep increases considerably at temperatures approaching T_g however, and patients may cause distortions of the denture by soaking dentures in boiling water. The use of water at temperatures above approximately 65°C should be avoided for soaking dentures. This is not only to ensure that the T_g of the resin is not approached but also the relief of internal stresses, accompanied by distortions, is minimized. The T_g value may be reduced to 60°C or lower if large quantities of low molecular weight material of residual monomer are present (McCabe and Walls, 1998).

Therefore it is crucial to measure the T_g of copolymer produced. In this experiment, DSC measurement was conducted at temperature range from 35°C to 250°C at heating rate of 10°C and 20°C/ min. Scan was done twice and result of T_g was taken from the second scan.

Table 3.12
Glass transition temperature obtained from DSC scans.

Macromer composition (wt %)	T_g of polymer (°C)	
	Bulk A	**Bulk B**
0	125	-
5	109	104
10	126	83
15	93	80
20	126	84
30	125	81
100	125	
Lucitone 199®	145	

T_g of Lucitone 199® is higher than any copolymer due to incorporation of certain amount of reinforcing fillers by the manufacturer.

T_g values are taken upon change in heat flow. DSC thermograms obtained showed that all the macromer-MMA copolymers have high T_g values of 81°C to 126°C (Figures 4.1 to 4.3 in appendices, page 121-123).

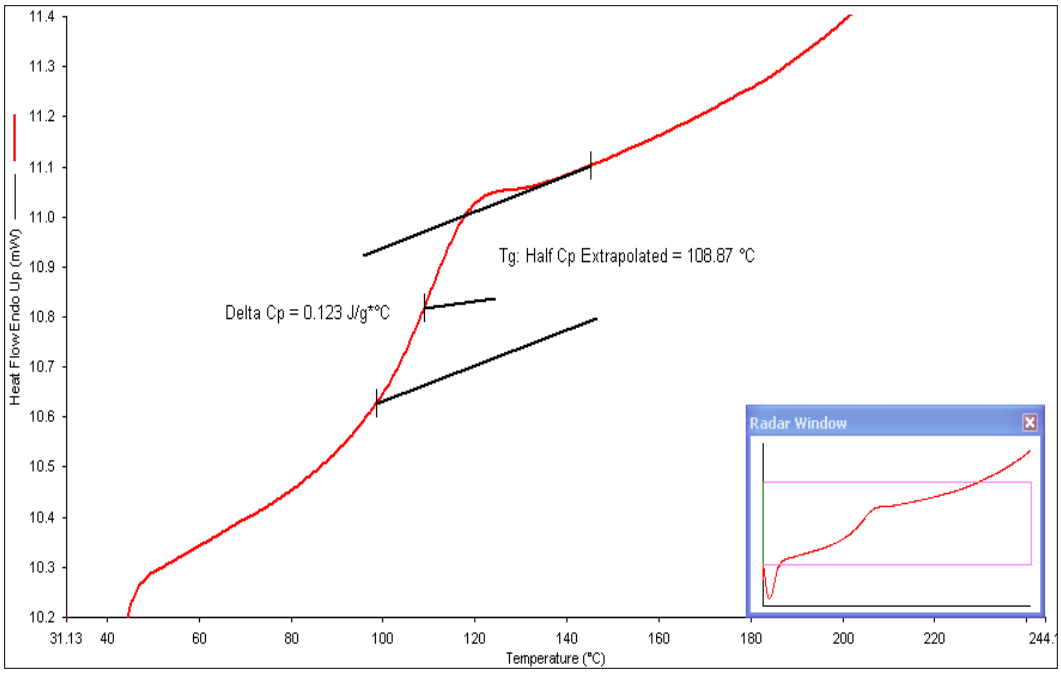


FIGURE 3.16 DSC thermogram of A5 copolymer.

For instance, Figure 3.16 shows the DSC thermogram of copolymer with 5 wt% addition of macromer and its T_g is 109°C which is considered high. The curing temperature of bulk copolymerization of 60-70°C overnight and 1 to 2 hours of terminal heat of 100°C was appropriate for the copolymer system.

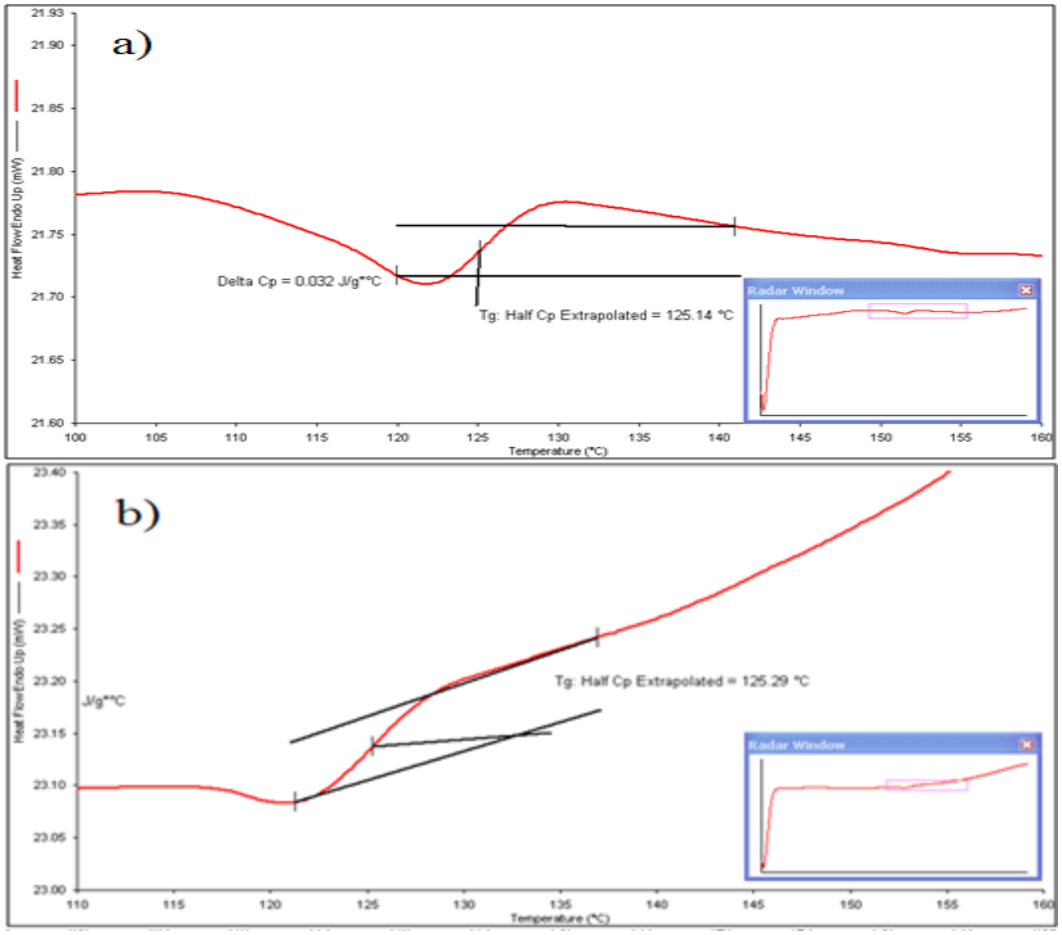


FIGURE 3.17 DSC thermograms of a) PMMA homopolymer b) Macromer.

The macromer and PMMA homopolymer themselves also have high T_g of both 125°C as shown in Figures 3.17 a) and b) respectively. PMMA formed in the copolymer system most probably was the atactic PMMA. The copolymerization of macromer with PMMA chain gives lower T_g copolymers compared to macromer and PMMA T_g values, as exhibited in Table 3.12. They decrease from 125°C to 108°C to 80°C. T_g values of A10, A20 and A30, highlighted in yellow color, are exactly the same as the macromer's and PMMA's probably due to the homopolymer or macromer part that existed in the samples.

Meanwhile, slightly lower T_g (81°C to 104°C) are observed in the Bulk B group of copolymers with crosslinking agent (Figures 4.2 – 4.3 as attached in pages 122-123). The cross-linker addition gives no significant difference in mechanical strength of the copolymers due to its low T_g compared to non-crosslinked copolymers as summarized in Table 3.12.

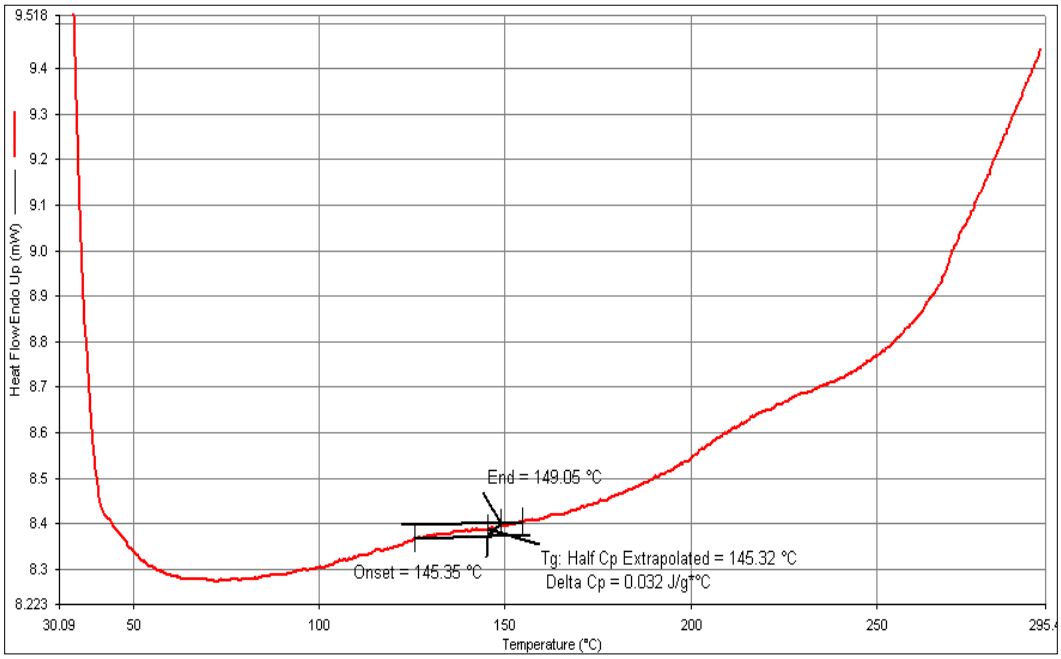


FIGURE 3.18 DSC thermogram of commercial resin, Lucitone 199®.

Figure 3.18 shows Lucitone 199® denture-base resin thermogram that has notably higher T_g value than any copolymers and PMMA itself, probably due to the presence of reinforcing filler added by the manufacturer.

3.4 Physical properties of copolymers

3.4.1 Water sorption and water solubility

Sorption values were expressed in two ways, which were microgram/mm^3 (Figure 3.19, page 90) and percentage of absorption (w/w) (Figure 3.20, page 91). The values for the water sorption, W_{sp} for each specimen, were calculated and expressed in micrograms per cubic millimeter (µg/mm^3) using the following equation:

$$W_{sp} = (m_2 - m_3) / V,$$

where m_2 : mass of the specimen (µg), after immersion in water

m_3 : reconditioned mass of the specimen (µg)

V : volume of the specimen (mm^3)

The values calculated for water sorption was rounded off to the nearest microgram per cubic millimeter (µg/mm^3). The sorption value also was calculated and expressed in percentage (w/w) as follows:

$$Sorption = (m_2 - m_1 / m_2) \times 100\%$$

The soluble matter per unit volume, W_{sl}, leached out during immersion, for each specimen was calculated and expressed in micrograms per cubic millimeter (µg/mm^3) as follows:

$$W_{sl} = (m_1 - m_3) / V,$$

where m_1 : conditioned mass of the specimen (µg)

m_3 : reconditioned mass of the specimen (µg)

V : volume of the specimen (mm^3)

Table 3.13
Physical properties of copolymers compared with the controls.

Sample	Sorption, μg/mm^3	Sorption, w/w%	Solubility, μg/mm^3
Homopolymer	12.83 (1.1)	1.35(0.1)	NA
A5	3.80 (0.3)	0.38(0.1)	0.39 (0.2)
A10	8.15(3.0)	0.90(0.3)	NA
A15	8.38(3.0)	0.58(0.3)	1.40 (0.5)
A20	15.39 (6.1)	1.65(0.6)*	NA
A30	24.52 (6.9)*	2.42(0.6)*	NA
B5	7.47(6.3)	0.34(0.1)	1.24 (0.1)
B10	7.12 (1.6)	0.54(0.2)	1.28 (1.1)
B15	11.84 (2.6)	0.97(0.3)	1.48 (0.2)
B20	9.56 (1.5)	0.76(0.1)	1.31 (0.1)
B30	11.52 (4.4)	0.73(0.1)	2.66 (1.2)
Lucitone 199®	6.75 (2.0)	0.71(0.2)	0.51 (0.7)

Values in parentheses are standard deviations.
*****shows significantly different value among group
NA: Values are not available.

Means of the sorption and solubility value of macromer-MMA copolymers, homopolymer and Lucitone 199® were calculated using SPSS version 12.0. One-way ANOVA analysis in Table 3.13 reveals that all sorption values are significantly different ($p<.05$). Therefore, Scheffé's post-hoc test was done to determine which group was significantly different from others. Comparing the sorption values of all groups with homopolymer and Lucitone 199®, the sorption value of A20 and A30 are significantly higher than others as expressed in Table 3.13. All copolymers of group A sorption values are not

significantly different with the respective copolymers of group B except for A30 and B30.

Figures 3.19 and 3.20 exhibit increased pattern of water sorption when the macromer composition is increased.

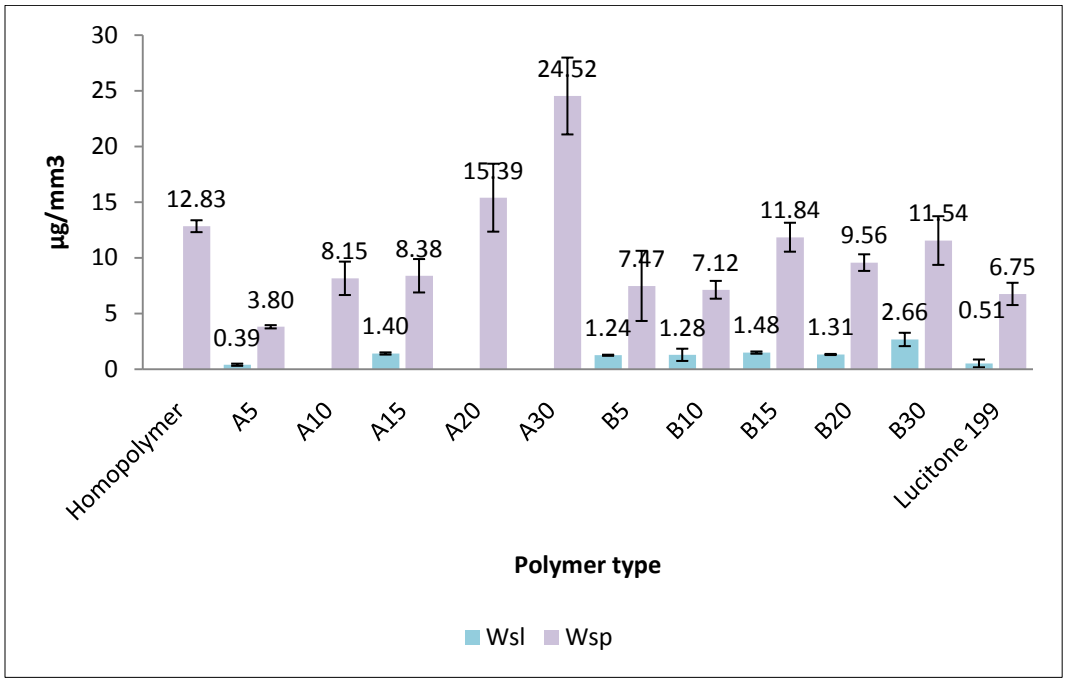


FIGURE 3.19 Sorption and solubility properties of homopolymer, copolymers and Lucitone 199® (µg/mm^3).

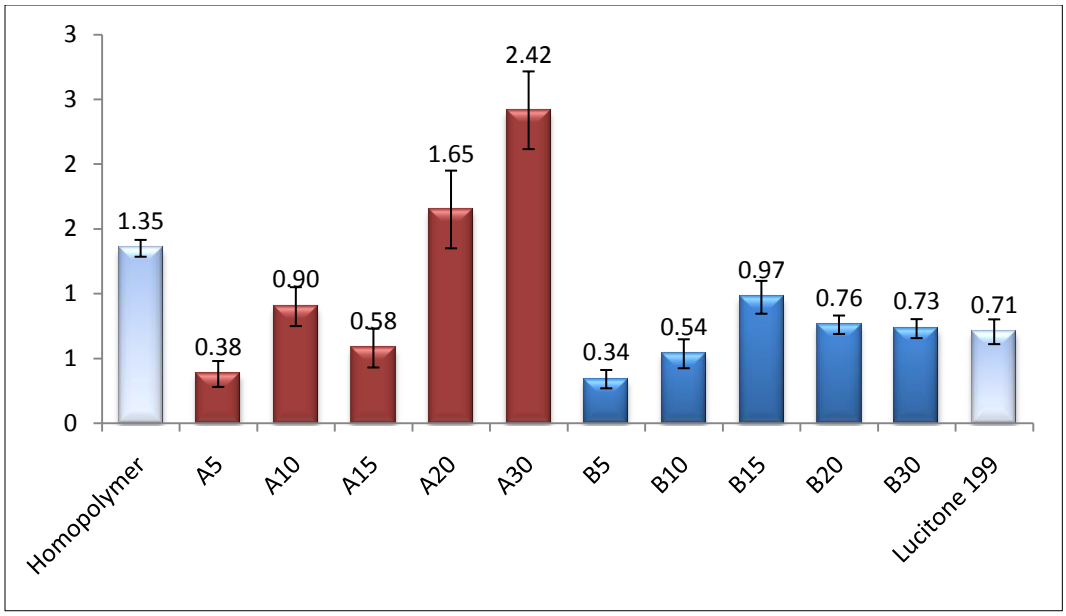


FIGURE 3.20 Sorption and solubility properties of homopolymer, copolymers and Lucitone 199® (w/w %).

In Figure 3.20, crosslinked copolymers of Group B showed relatively low water sorption than non-crosslinked copolymers of Group A and the homopolymer. All copolymers showed promising properties of low water sorption when addition of macromer was no more than 20% w/w.

One-way ANOVA analysis reveals that all the solubility values are significantly different (p=.05). Therefore, Scheffé's post-hoc test was done to determine which group is significantly different from others. Comparing the value of solubility of all groups with Lucitone 199®, sample B30 has significantly higher solubility value compared to others. Value of water solubility for homopolymer, sample A10, A20 and A30 however are not obtained (Table 3.13). This observation is probably due to the discs that were not totally dried when measurements were taken.

DISCUSSION

Amongst the undesirable physical properties of denture base polymer are the water absorption and water solubility. Denture base polymers absorb water slowly over a period of time when immersed in an aqueous environment. Water absorption by denture base resin commences during the processing of a denture, followed by polishing and storing of dentures in water before insertion in the mouth. This process continues during the clinical stage (Chau and Ting, 2007).

When samples are immersed in water, little or no increase in the volume of the polymer specimen occurs. This process is explained as absorption in 'microvoids' (Arima et al., 1995). The absorption of water derives mainly from the polar properties of resin macromolecules through a diffusion process (Chau and Ting, 2007). Macromer chain itself has hydroxyl groups that could possible form hydrogen bonding with water resulting in water sorption.

Water taken up into the material acts as a plasticizer thus affects the mechanical properties. In addition, water sorption can also cause dimensional change (Arima et al., 1995). Therefore, it is crucial to ensure that the copolymer absorbs minimum or least water. Acrylic resin slowly absorbs water and an equilibrium value of about 2% absorption is reached after a period of several days or weeks depending on the thickness of the denture. Loss or gain of water in the surface layers may occur quite rapidly and this is the fact that contributes towards crazing (McCabe and Walls, 1998). The experimental copolymer produced

showed water sorption ranging from as low as 0.4% w/w to as high as 2.4% w/w in seven days of soaking in water.

The solubility of acrylic resins represents the amount of water-soluble ingredients, un-reacted monomers, plasticizers and initiators that leached out during the seven days the specimens were immersed in water (Cucci et al., 1998).

Methacrylate polymer is not soluble in water, and therefore the water solubility figure represents the mass of soluble materials, un-reacted monomers, plasticizers and initiators. These may gradually leach out of the polymerized material and sometimes produce a soft tissue reaction (Arima et al., 1995). The solubility value of the copolymers increased with increase in the addition of macromer. This suggests that the soluble part that leached out were parts of un-reacted alkyd chain that were in excess.

When the processed polymer was tested in accordance with standard procedure ISO 1567 Denture Base Polymers, the increased volumic mass (water sorption) shall not exceed 32 $\mu g/mm^3$ and the loss in volumic mass shall not exceed 1.6 $\mu g/mm^3$. Thus all copolymers tested passed the ISO requirements for water sorption and solubility limit. Only sample A30 has failed, which has solubility value exceeds 1.6 $\mu g/mm^3$.

3.5 Flexural and Impact properties of copolymers

PMMA is not ideal as a denture base because it is susceptible to fracture as a result of fatigue failure, excessive masticatory forces or an impact onto hard surface (Carlos and Harrison, 1997). There have been many attempts to improve the PMMA and they are adopting one of the two following approaches. The first approach is to increase the strength of polymer by adding cross-linking agent of poly-functional monomer such as polyethylene glycol dimethacrylate. The second approach is to reinforce the polymer with fibers or rods (Kanie et al., 2000).

The resistance to fracture of acrylic resin dentures depends on, among other factors, flexural strength and impact strength. The former gives an indication of material performance under conditions of static loading while the latter involves testing under dynamic loading conditions and involves a measure of energy absorbed by the material before fracture (Robinson and McCabe, 1993).

In this study, the first approach was used. The unsaturated macromer acts to form grafting or networks with the PMMA chain and will modify the mechanical properties of PMMA. Two mechanical testings were performed, namely flexural test or three-point bend test and Charpy-notched impact test. Flexural strength is stress at fracture using this method of testing. This method is to replace tensile test for evaluation of brittle materials. Impact strength is degree of resistance of polymeric material to impact loading (Callister, 2003). It also represents the total energy absorbed by a material before it fractures, when struck

by a sudden blow from an impact instrument with a weighted pendulum (Faot et al., 2006). From flexural test, flexural strength and modulus elasticity of the copolymers were obtained along with the deflection point where the material broke into two pieces (specimen failure point). Impact strength was obtained from the impact test.

Table 3.14
Flexural strength, modulus of elasticity, deflection at specimen failure and impact strength of copolymers compared to homopolymer and commercial resin.

Sample	Flexural strength, MPa	Modulus of elasticity, GPa	Deflection at yield (Maximum load), mm	Impact strength, kJ/m^2
Homopolymer	79.5(18)	2.18(0.3)	4.13(1.2)*****	0.8(0.4)*****
A5	90.8(7)	2.73(0.2)*****	5.6(1.6)	3.6(0.5)
B5	70.8(9)*****	2.08(0.4)	6.4(1.9)	1.6(0.5)*****
A10	89.9(5)	2.56(0.2)	6.6(1.3)	2.5(0.5)
B10	83.1(10)	2.41(0.3)	6.6(1.9)	2.1(0.5)*****
A15	69.9(7)*****	2.12(0.2)	7.3(0.5)*****	1.6(0.4)*****
B15	71.5(5)*****	2.14(0.3)	6.6(1.0)	1.6(0.3)*****
A20	60.0(8)*****	1.83(0.3)	6.8(0.9)	1.3(0.4)*****
B20	52.8(7)*****	1.62(0.2)*****	6.7(0.9)	1.5(0.4)*****
A30	39.6(8)*****	1.12(0.2)*****	6.9(1.7)*****	1.0(0.5)*****
B30	42.0(2)*****	1.30(0.1)*****	5.4(0.8)	1.9(0.5)*****
Lucitone 199®	93.8(10)	2.27(0.2)	7.6(1.5)*	3.2(0.7)

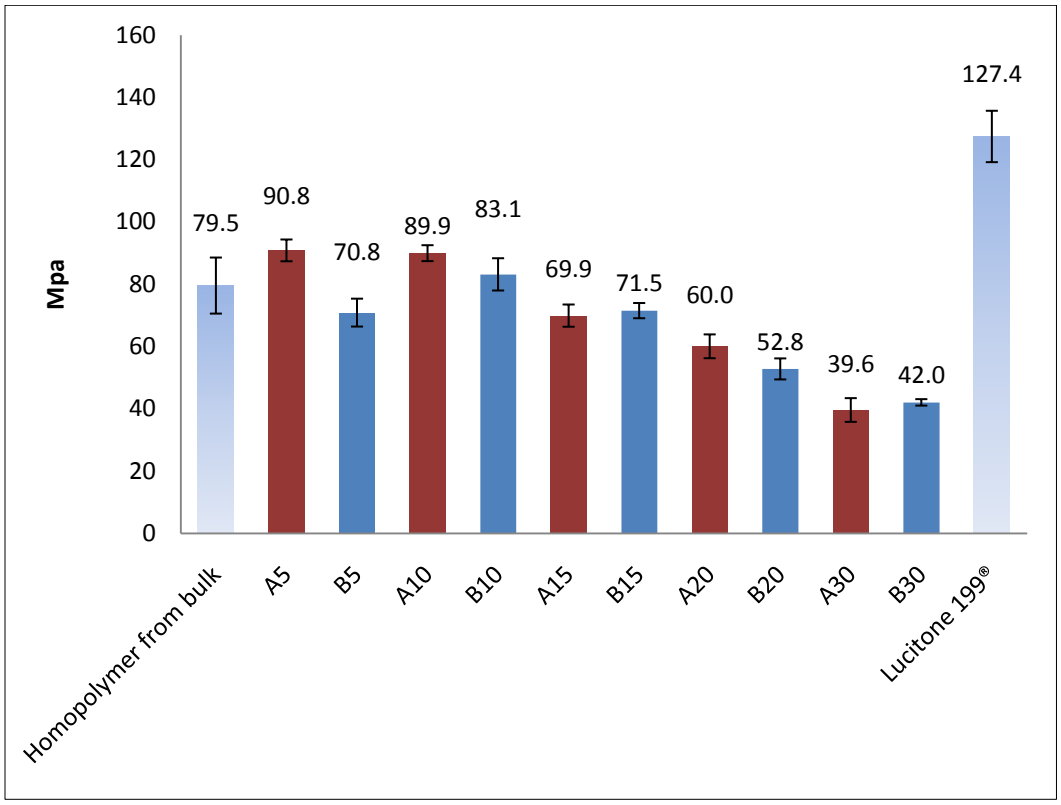
Values in parentheses show standard deviation.
*Shows significant difference of the item among its group of each parameter.

Table 3.14 summarizes the mechanical testing results. All mean values show significant difference of each other after statistical analysis of variance (ANOVA) therefore Scheffé's post-hoc test was conducted afterwards.

Flexural strengths of all copolymers are significantly lower from flexural strength of Lucitone 199® (control), except for PMMA homopolymer made from bulk technique and copolymers A5, A10 and B10. The flexural properties of these copolymers are quite good. For non-crosslinked copolymers of A group, the flexural strength of homopolymer increases to 79.5 MPa (18) and copolymer's values range from 39.6 MPa (8) to as high as 90.8 MPa (7) as referred in Table 3.14. Meanwhile, the strength of Lucitone 199® is 93.8 MPa (10). These significantly different values are due to the fact that Lucitone 199® was a commercial resin with fillers and additives, therefore exhibits high values of flexural strength. They contain about 70 wt% of PMMA pre-polymer powder as filler, with only 30 wt% of liquid MMA monomer and unspecified amount of EGDMA as a cross-linking agent. The bulk copolymers whereas were made with 70 to 95 wt% of liquid MMA and contained no PMMA pre-polymer filler. Addition of 5 to 30 wt% unsaturated macromer was to copolymerize and crosslink with MMA.

Addition of 0.25 w/w% EGDMA as a cross-linking agent in Group B copolymers, shows no significant difference in their flexural strength ($P>.05$) compared to their respective non-crosslinked A group copolymers. EGDMA

addition somehow has lowered the flexural strength value of each non-crosslinked copolymer of Group A (Table 3.13) except for copolymer with 30 wt% macromer addition. 20 wt% (A20 and B20) and 30 wt% addition (A30 and B30) of macromer into the copolymer clearly has decreased the flexural strength of the copolymers. This observation is re-illustrated in Figure 3.21.



All copolymers of A and B groups are of bulk copolymerization.

FIGURE 3.21 Flexural strength of non-crosslinked (Group A) and crosslinked (Group B) copolymers compared to controls.

Flexural strength of non-crosslinked (Group A) and crosslinked (Group B) copolymers with macromer addition of less than 20% are considered high and comparable with PMMA homopolymer but relatively lower than the commercial resin. However, there is no significant difference between these two groups.

From Table 3.14, the impact strengths of all copolymers also show significant differences when compared to the strength of Lucitone 199®, except for copolymers A5 and A10. For non-crosslinked copolymers, the impact strength values were 30% to 300% higher than the homopolymer. Copolymers incorporated with 5 and 10 wt% of macromer have met the requirement of the ISO standard, which is 2.0 kJ/m^2. Incorporation of 5 wt% macromer into the copolymer system yield highest impact strength which is 3.6 kJ/m^2 (0.5) and further increase of macromer in the copolymer system has decreased the impact strength down to 1.0 kJ/m^2 (0.3) but it is still higher than the homopolymer.

For crosslinked copolymers of Group B, no significant increase is observed with the addition of crosslinking agent. B5 and B10 impact values are lower than A5 and A10 while A15 and B15 share the same impact strength value. Further addition however does increase the impact strength value to 1.9 kJ/m^2 (0.5) but the increase is not significantly different ($p>.05$). Figure 3.22 summarizes the impact strength of copolymers and it reflects quite similar pattern as in flexural strength.

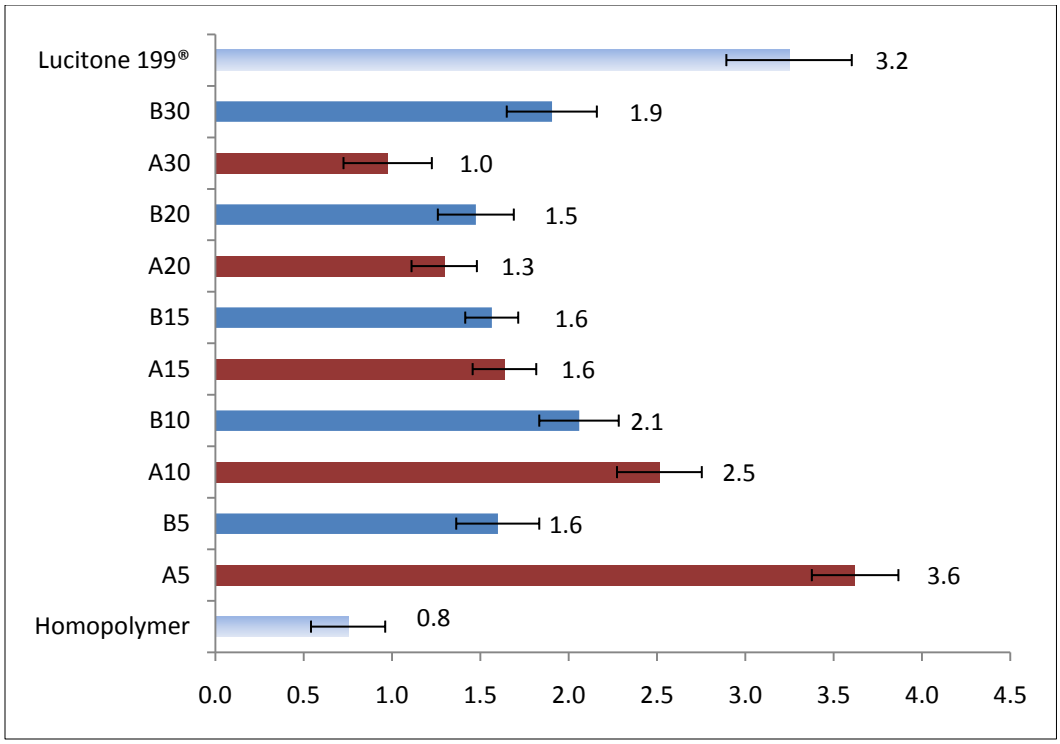


FIGURE 3.22 The impact strength of PMMA homopolymer increased. Further addition of macromer beyond 10% w/w progressively lowers the impact strength of the copolymers.

Modulus of elasticity is the ratio of the stress to the strain for a given stress. The greater the modulus, the stiffer the material will be, and considerable stress must be induced before a notable strain or deformation results (Uzun et al., 1999). In this test, A5 copolymer shows significantly high modulus of elasticity when compared to the control polymers (homopolymer and Lucitone 199®) while copolymers B20, A30 and B30 show significantly smaller difference value from this control polymers (Table 3.14).

The deflection values show that homopolymer experiences the least deformation before fracture (Uzun et al., 1999). The greatest permanent deformation is exhibited by Lucitone 199® followed by A15 and A30 (Table 3.14).

Overall, PMMA homopolymer and copolymers A5, A10 and B10 have high flexural and impact strengths. However the copolymers that met ISO requirements for flexural and impact strength are PMMA homopolymer and copolymers A5, A10, B10, A15 and B15. Further increase of macromer addition results in high level of cross-linking or interpenetrating networks, which cause the copolymer to be less flexible and more brittle, therefore having low flexural and impact strength. This is why the addition of macromer was limited at 30%. Addition of EGDMA may have promoted crosslinking around PMMA chain alone and probably more macromer chain was left un-copolymerized.

In conclusion, the addition or copolymerization of macromer with MMA chain may have increased the impact and flexural strengths of PMMA homopolymer but still they are lower than the commercial resin tested. Further studies on how to increase the grafting or modify the hydroxyl groups of the macromer chain may improve the mechanical properties of the copolymers. Fillers and additives also could be incorporated in the copolymer system.

3.6 Morphology study of copolymers, homopolymer and commercial resin

3.6.1 Digital microscopy analysis

Visual inspection revealed that the macromer-MMA copolymers, PMMA homopolymer and the commercial resin have brittle fracture type. All the copolymers fractures exhibit well-defined, flat, compact and organized surface fractures as shown in Figure 3.23 and Figure 3.24. When fragment A (FA) (one of two parts that has been broken) and fragment B (FB) (the other part) could be repositioned at the fractured line, presenting a smooth surface, the fractures are classified as brittle. Those presenting plastic deformation, exhibiting rough and jagged surfaces, are recorded as intermediate (ductile-to-brittle transition) (Faot et al., 2006). During visual inspection, all the fragments FAs and FBs could be repositioned at the fractured lines, presenting a smooth surfaces, therefore are classified as brittle.

Figure 3.23 shows flexural and impact fracture of the controls. White arrow in Figure 3.23 f) shows the direction of impact load while black arrow shows the origin line of notch angle. All fragments demonstrate smooth lines with no plastic deformation, after repositioned. Thus fractures are categorized as brittle fracture.

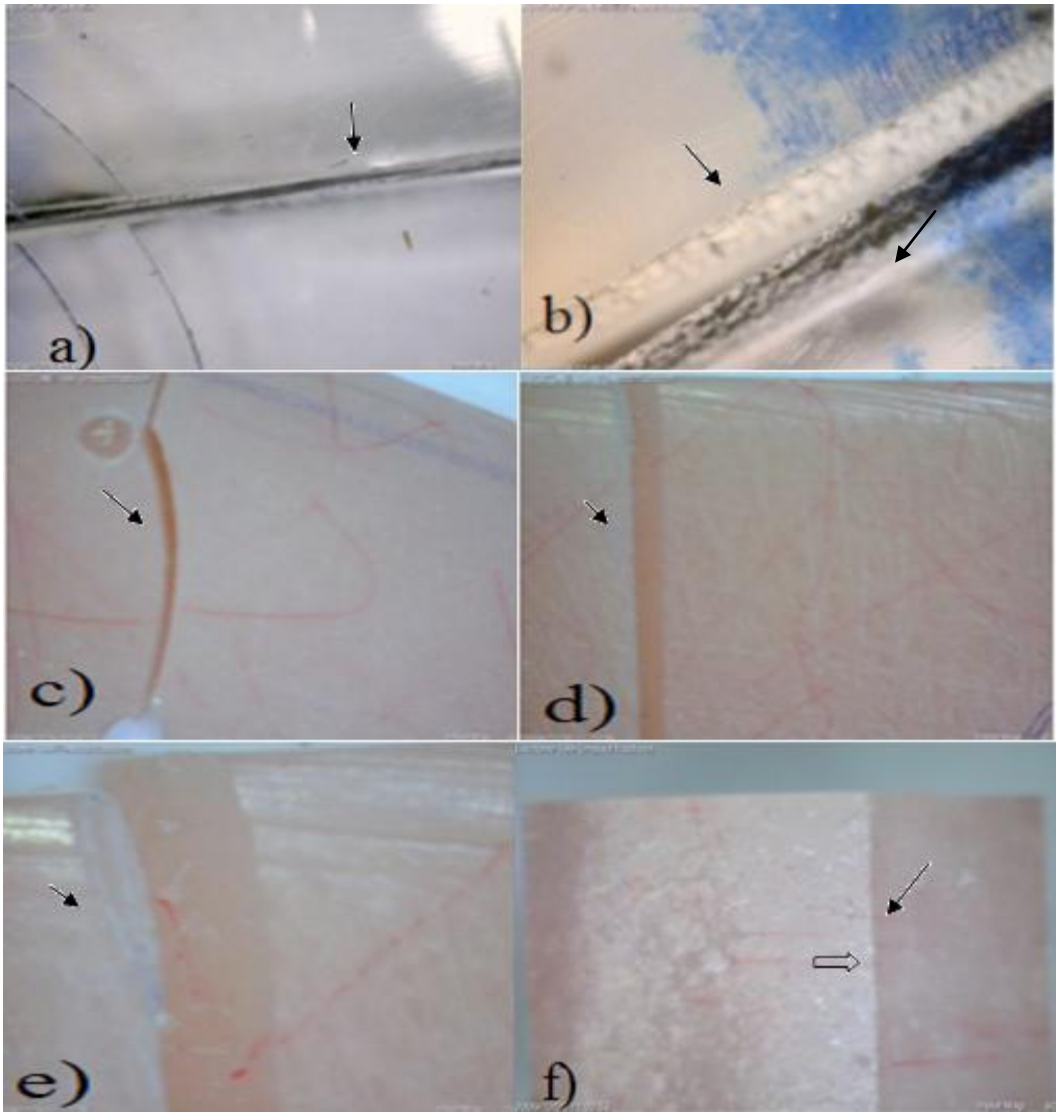


FIGURE 3.23 Flexural fractures of homopolymer of a) 70X and b) 200X magnification c) Lucitone 199® of 70X and d) 200X magnification e) Impact fracture of Lucitone 199® of 70X and f) 200X magnification.

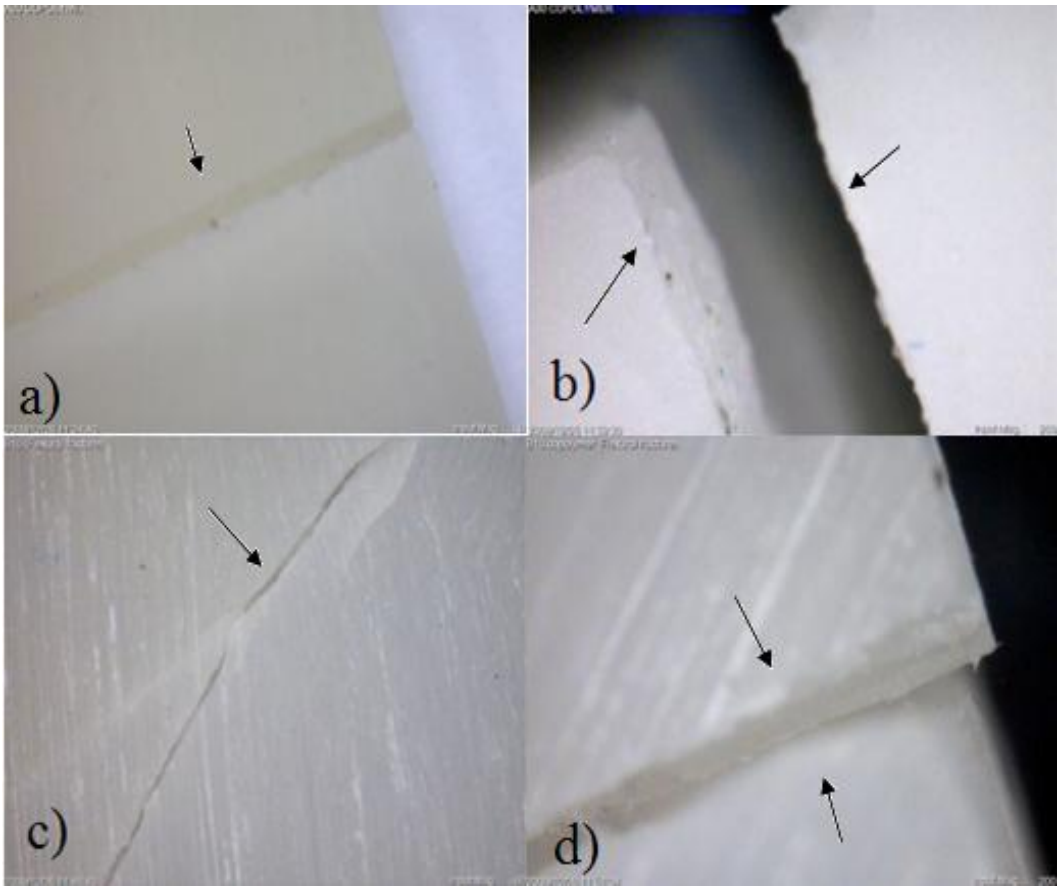


FIGURE 3.24 Flexural fractures of A30 copolymer of a) 70X and b) 200X magnification c) B10 copolymer of 70X and 200 X magnification.

Figure 3.24 a) to d) shows flexural fractures of non-crosslinked and crosslinked copolymers. All FAs and FBs, also demonstrate smooth lines with no plastic deformation like the controls, after repositioned. All black arrows show the fracture lines.

3.6.2 **The SEM analysis**

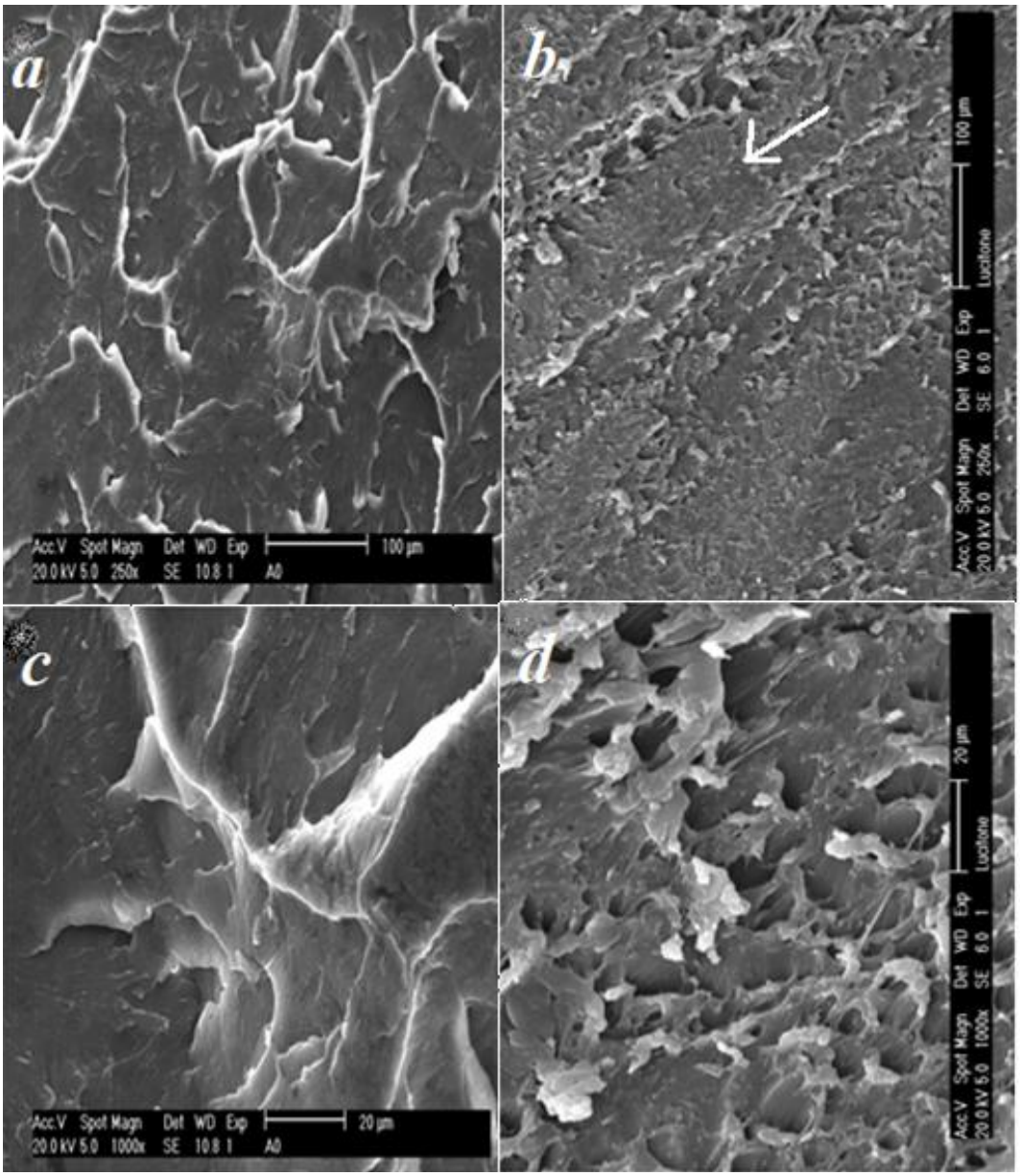


FIGURE 3.25 SEM micrographs of polymers fractured surface a) PMMA homopolymer (250X) b) Lucitone 199® (250X) c) PMMA homopolymer (1000X) b) Lucitone 199® (1000X).

Fracture of PMMA homopolymer in Figure 3.25 a) shows layered pattern ranging from 40 µm to 100 µm in diameter. Figure 3.25 b) shows image of

Lucitone 199® which exhibits half-cylindrical-crater-like appearance in the direction of bending load which is shown with white arrow. Further zooming in the fracture reveals that both control polymers have compact bases that explain the strong flexural strength when compared to experimental copolymers.

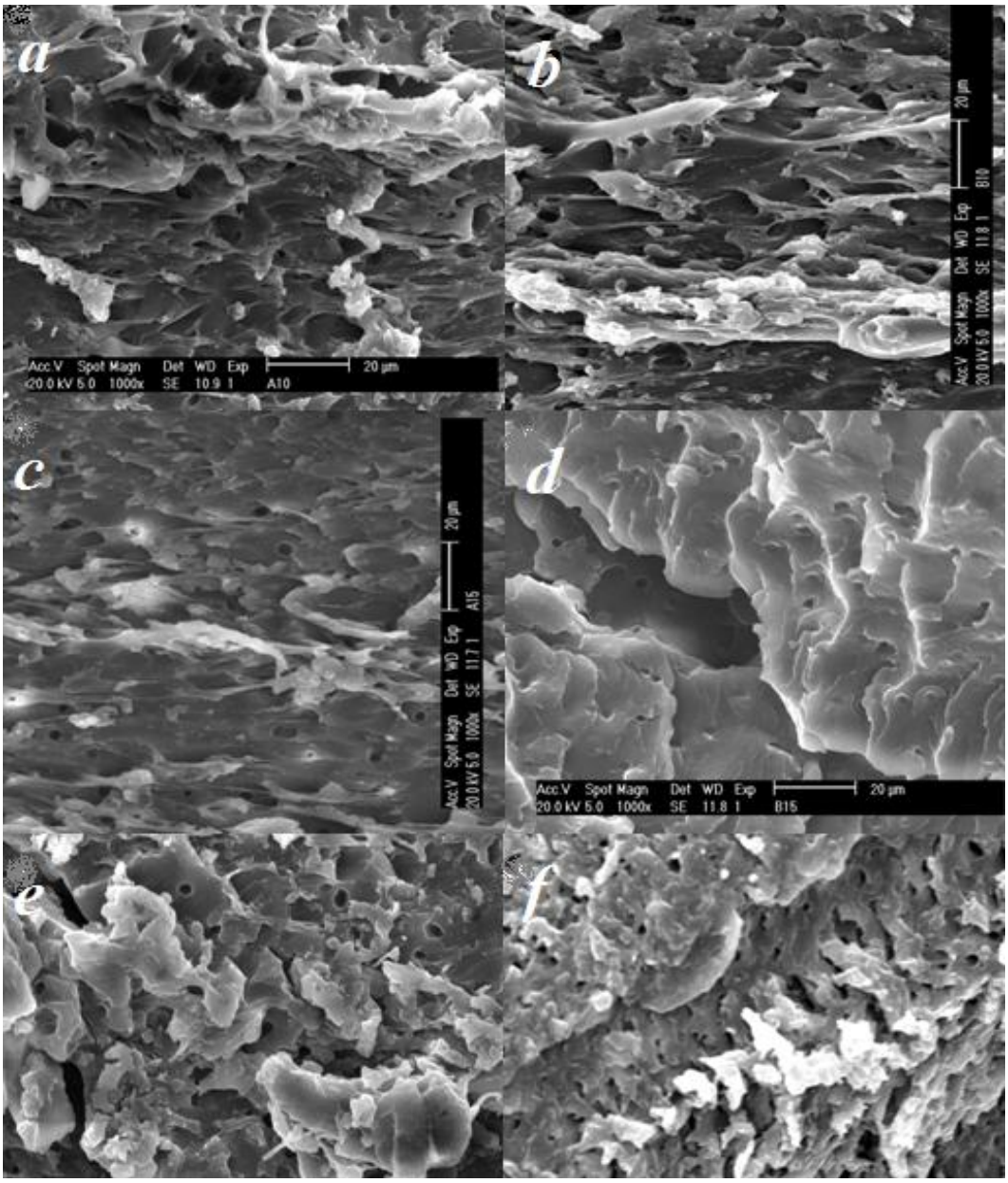


FIGURE 3.26 SEM micrographs of non-crosslinked copolymers (1000X magnification) a) A10 c) A15 e) A30 and crosslinked copolymers b) B10 d) B15 f) B30.

Figure 3.27 compares the non-crosslinked copolymers of A10, A15 and A30 with cross-linked copolymers of B10, B15 and B30. No significant difference was observed between these types. High magnification of SEM images

reveal that no micro pores are present, explaining the high flexural strength they exhibited relative to solution technique copolymer.

CHAPTER 4

CONCLUSION

4.5 Summary

Free radical copolymerization of FA35 unsaturated macromer with methyl methacrylate monomer were carried out using two different methods which were solution and bulk polymerization methods. While the solution copolymerization process was done at 80°C and 90°C, the bulk method was carried out at 60-70°C.

Each copolymer exhibited one T_g, indicating that both macromer and MMA was compatible. FTIR analysis showed characteristic peaks of both co-monomers (macromer and MMA). Addition of crosslinking agents did not significantly affect the T_g of the copolymers. All copolymers showed good thermal stability up to 160°C and 180°C before they started to degrade.

Evaluation of macromer-MMA copolymer as a denture base material showed promising properties of low water sorption when addition of macromer was below 20% w/w.

Mechanical tests revealed that the incorporation of macromer with MMA had improved the impact and flexural strengths. However, further addition of macromer beyond 15% w/w progressively lowered the mechanical strength of the copolymers.

4.6 Significance of some findings

In this work, the experimental copolymers contained a significant proportion of non-petroleum based material derived from palm oil. Incorporation of unsaturated FA35 macromer has increased the mechanical strength of acrylic resin.

4.7 Suggestions for further studies

Further tests need to be done in order to establish the copolymers as a denture base material, such as residual monomer content and biocompatibility test. The mechanical strength of the macromer-MMA copolymer could be enhanced by reaction of the hydroxyl groups in the macromer with other groups such as isocyanides. Incorporation of strengthening fillers could further modify the mechanical properties.

4.8 Published works

In Press: Progress in Polymer Research.

Nurshafiza Shahabudin, Gan Seng Neon, Noor Hayaty Abu Kasim.
Copolymers of methyl methacrylate and a palm oil-based alkyd for application as dental materials.

Abstracts

Shahabudin N, Abu Kasim NH, Gan SN (2008).
Flexural strength of PMMA modified with palm oil-based polyol.
J Dent Res 87B, Abstr.3179, 2008 (www.dentalresearch.org).

Shahabudin N, Abu Kasim NH, Gan SN (2008).
Modification of PMMA dental resin with palm oil-based polyol.
J Dent Res 87C, Abstr.0086, 2008 (www.dentalresearch.org).

Conference proceedings

1. Nurshafiza Shahabudin, Gan Seng Neon and Noor Hayaty Abu Kasim, *Modification of polymethyl methacrylate by a palm oil-based macromer*- 16th Malaysian Chemical Congress, 12-14 October 2010, Putra World Trade Centre, Kuala Lumpur, Malaysia- Poster # MPC36P.

2. Nurshafiza Shahabudin, Gan Seng Neon, Noor Hayaty Abu Kasim, *Synthesis and Mechanical Properties Evaluation of Methyl Methacrylate Copolymer with Palm Oil based Polyester* – Malaysia Polymer International Conference, 21-22 Oktober, 2009, Putrajaya, Malaysia – Oral presentation #PC03.

3. Nurshafiza Shahabudin, Gan Seng Neon, Noor Hayaty Abu Kasim, *Flexural Strength of PMMA Modified with Palm Oil Based Polyol*, 25 June 2008, Department of Chemistry Mini symposium, Faculty of Science, UM – Oral presentation.

4. Nurshafiza Shahabudin, Gan Seng Neon, Noor Hayaty Abu Kasim,*Transverse Strength of PMMA Modified with Palm Oil Based Polyol*, 28 February 2008, International Association of Dental Research (IADR) – Malaysia Section, Faculty of Dentistry, UiTM Shah Alam- Poster presentation.

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APPENDICES

LIST OF MATERIAL, INSTRUMENT AND MANUFACTURER

DSC THERMOGRAMS

SECTION I

Table 4.1
List of Material, Instrument and Manufacturer cited in text

No.	Item	Manufacturer
1	Analytical balance	Denver Instrument Co., USA
2	Benzoyl peroxide	Sigma-Aldrich, Germany
3	Diamond Precision Sawing Machine	Buehler, Germany
4	Digital Microscope	Dinolite, AnMo Electronics Corporation, Taiwan
5	EGDMA	Sigma-Aldrich, Germany
6	FTIR-ATR Spotlight 400	Perkin Elmer, USA
7	FTIR Spectrum RX Series	Perkin Elmer, USA
8	Grinding and polishing machine	Buehler, Germany
9	Impact Pendulum	RayRan, Warwickshire, United Kingdom

Table 4.1 continued

10	Lucitone 199®	Denstply Trubyte, USA
11	MMA	Merck &Sigma-Aldrich, Germany
12	Mitutoyo digital vernier calliper	Mitutoyo Ltd., Tokyo, Japan
13	Motorized Notch Cutter	RayRan, Warwickshire, United Kingdom
14	Pyris 6 TGA	Perkin Elmer, USA
15	Pyris /Diamond Thermogravimetric/Differential Thermal Analyzer DSC	Perkin Elmer, USA
16	Scanning Electron Microscopy	Phillips XL series, Midland, ON, Canada
17	SPSS version12.0	SPSS Incorporated, Chicago, USA

SECTION II

DSC thermogram of polymers

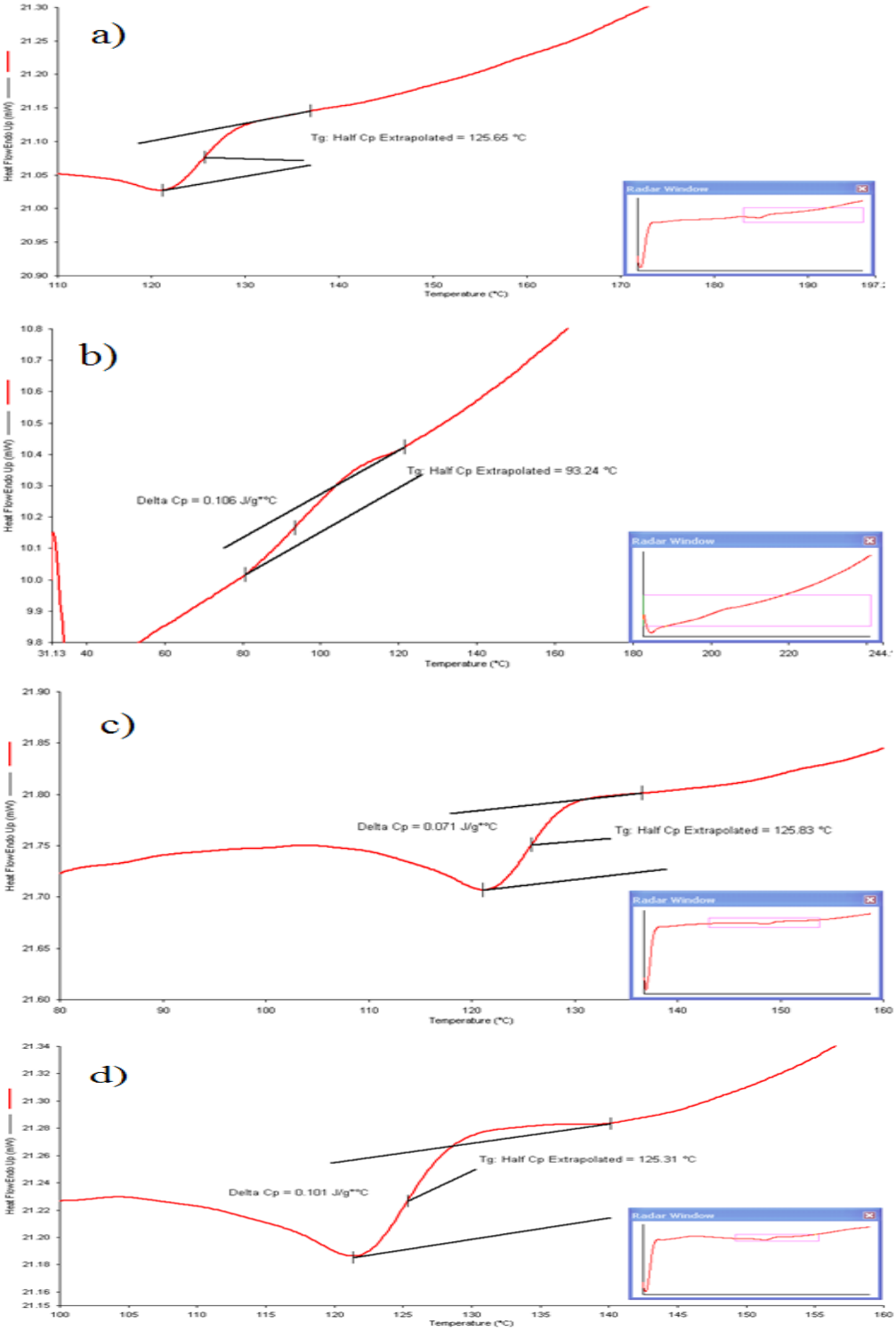

FIGURE 4.1 DSC thermograms of non-crosslinked copolymers a) A10 b) A15 c) A20 d) A30

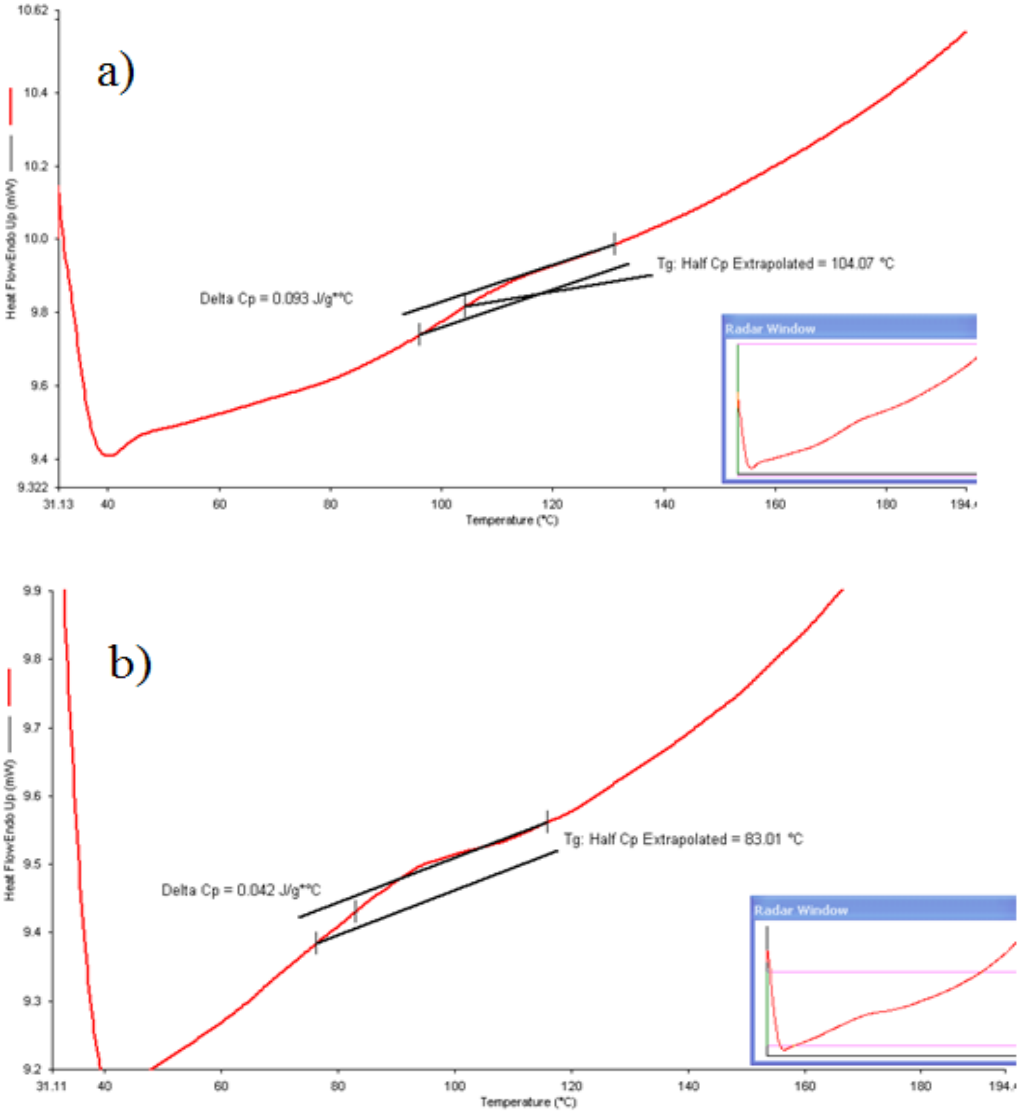

FIGURE 4.2 DSC thermograms of crosslinked copolymers a) B5 b) B10.

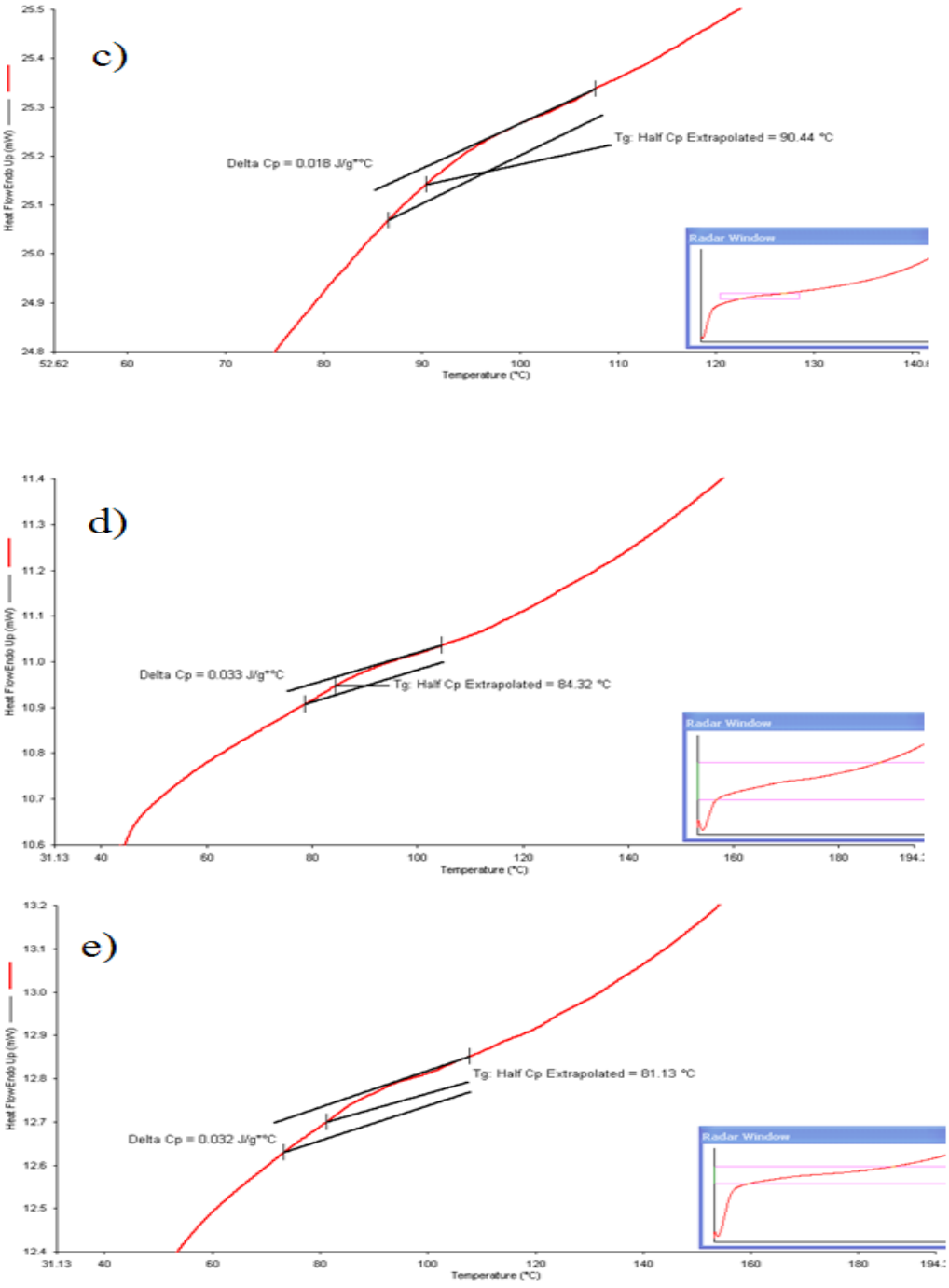

FIGURE 4.3 DSC thermograms of crosslinked copolymers c) B15 d) B20 e) B30.